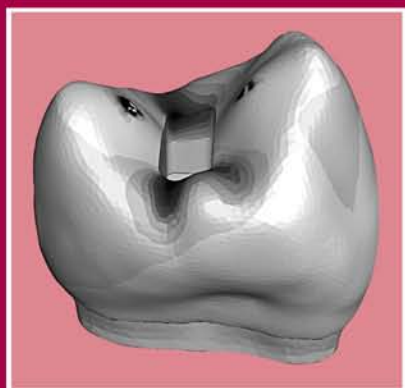




Dental biomaterials

Imaging, testing and
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Richard V. Curtis and Timothy F. Watson

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Preface

The dental and biomaterials science literature is full of excellent research papers that give mention to many exciting techniques for the determination of physical properties, chemical constituents and structural organisation of biomaterials and their biological substrates. Equally, there are review papers that look at materials from the clinical perspective without probing the materials and biological background in depth. However, there are very few sources of information available to the researcher who is setting out in a new field of study, who wants to be updated in a particular area of newly developing technology or who wants to give their postgraduate students a source of primary information for their studies of the literature. *Dental biomaterials: imaging, testing and modelling* may help to redress this balance.

When assembling the list of authors for this book we aimed to incorporate individuals who are the leaders in their respective fields in dental biomaterials. The authors are from many different backgrounds and elegantly illustrate the profitable results of collaboration between the laboratory and the clinic. There is no doubt that there are many areas of endeavour that have not been covered in this present edition, but a book can only be a finite size. We hope that the collection of chapters covers a suitably wide-ranging suite of topics and that it may encourage individual researchers to look to other, parallel, technologies to their own and so advance the exciting world of dental biomaterials science.

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Characterizing the performance of dental air-turbine handpieces

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1.1 Outline

After briefly outlining the general importance of air-turbine handpieces in dentistry (Section 1.2), a historical account of their development puts their present status into context (Section 1.3). However, in order to understand performance in general, it is necessary to recognize the large number of factors involved, and their complex interactions (Section 1.4). In essence, it is not yet possible to characterize the cutting performance of these devices, dependent as they are on the behaviour of cutter and substrate, amongst other things. Accordingly, it is as yet only feasible to document the physical aspects of the behaviour of the turbine itself (Section 1.5), but this leads to a number of figures of merit that may be used for product comparisons in an objective fashion that are tied to the physics of these machines. Even so, because of their internal complexity, primarily in terms of gas flow, it is necessary to resort to the ‘black-box’ approach and document input–output relationships, subsuming much unresolvable detail in some fitted parameters. Selection and application by the end-user nevertheless depends on a number of further issues of great importance, and these are discussed under the general heading of hazards (Section 1.6). The chapter closes with some general remarks on selection, usage, and areas where further study is essential.

1.2 General importance: applications, benefit

The dental air-turbine handpiece rapidly gained widespread acceptance by the dental profession after its introduction in the late 1950s, and it continues to be used as the main means of carrying out cutting work in clinical dental practice, whether of tooth tissue or restorative materials. In comparison with alternatives at the time, the reasons given for its usefulness included the following.

- Power: power-to-weight ratio very favourable, negligible transmission loss;

- Size: size and weight allow better control for long periods without tiring as well as good intraoral access;
- Speed: reduction of unpleasant vibration, finer control of cutting process;
- Effort: lower forces could be used yet with higher removal rates.

These considerations still appear to be pertinent.

1.3 Historical outline: development, features

A turbine is a motor in which a shaft is steadily rotated by the action of a current of fluid upon the blades of a wheel. Turbines powered by various fluids have evolved along several paths, and it is not possible to identify a single source for the development of dental systems.

The first air-powered dental engine design was patented in 1868¹ although in fact this was not a turbine but effectively a lobe pump operated in reverse. It was intended to be operated by mouth, foot bellows, or a compressed air vessel. The first true turbine dental handpiece, with a 13-bladed rotor, was patented in 1874,² with similar suggestions for operation as the lobe pump. It received little attention from the profession. A water-powered device in 1877³ also made provision for a fine stream of water to be directed as coolant onto the cutting instrument. A more elaborate device with a transmission clutch, a rotatable handpiece sheath, and revised mechanism for the attachment of cutting instruments followed in 1879,⁴ although details of the turbine rotor were not given and the drive fluid was not specified.

These machines were all somewhat bulky with their weight borne by the dentist's hand. However, a water-powered engine, produced by S. S. White in 1881⁵ avoided this problem by the motor being mounted on a floor stand. A flexible shaft transmitted the drive in a fashion similar to that of many foot-treadle engines of the time. Evidently, the problems were greater than the advantages. Improvements made to foot-treadle and electric dental engines in the late 1800s led to fluid-driven devices falling by the wayside and, by the 1920s, the cord-arm drive had been adopted as the *de facto* standard means of transmission from an electric motor to the handpiece.⁶

In the 1870s, the maximum speeds were around 700rpm (12/s) and 1000rpm (17/s) for foot-driven and electrical devices, respectively.⁷ Speed, recognized to be beneficial, progressively increased, but success depended in part on suitable rotary cutting instruments being available, as well as improved means of cooling the cutting site. An electric engine of 1911 reputedly achieved up to 10000rpm (167/s),^{6,8-10} separating discs and grinding tools worked more smoothly with less patient discomfort. However, the engine was unsuccessful because of overheating and seizure of the hand-

piece bearings.^{6,9} Effective means of achieving such speeds did not become available until the 1940s.

Studies of vibration perception provided evidence in favour of increased speeds.^{11–13} The upper frequency threshold of vibration perception was found to be ~650 Hz, with maximum unpleasantness in the range 100–200 Hz. Using burs, stones, and diamond instruments at 3000–4000 rpm (50–67/s), the vibrations produced were ~110–150 Hz. An air-turbine handpiece was then developed (see below) specifically to produce vibrations above the limit of perception by virtue of its high rotation rate. In the end, it was concluded that, in procedures that resulted in the same range of temperature rise, high-speed devices could remove enamel some three times as fast and at 1/30th of the operating load, as well as with better control and less effort.¹⁴ Indeed, with proper cutting-site cooling, high-speed rotation was not only possible but practical, safe, and effective,^{15,16} with advantages for both patient and operator.¹⁷ In fact, it was said that ‘few pieces of equipment in dentistry have caused more changes and improved dental service to a greater degree than ultra-high-speed handpieces (i.e. those rotating at 1000–5000/s),’¹⁸ allowing improved patient response, shortened operating time, reduced vibration perception, and less patient and operator fatigue. For these reasons this development was described as ‘one of the most significant contributions to dental health service’.¹⁹

Nevertheless, high-rotation-rate cutting only became possible when instruments became available that could withstand such speeds. Until at least 1870, steel burs were the only cutting instruments available and these were individually shaped and finished by hand. The mass production of carbon steel burs began by the 1870s.⁸ Corundum (Al_2O_3) separating discs and stones were introduced in 1872^{6,8,9} and provided the first satisfactory means of cutting enamel, although subsequently supplanted by carborundum (SiC).

Diamond grit cutting instruments were first advertised in 1878²⁰ but, being on a soft copper core, could not be used at high speed until the development in 1932 of galvanized bonding to harder alloy.^{6,8,9} Tungsten carbide burs followed in 1948 and proved to be extremely successful in high-speed applications.⁸ There has been no significant development since then.

The problem of heat generation remained, although recognized as much as 2000 years ago²¹ for surgical trephines. A cooling system was fitted to one handpiece in commercial production by 1874:²² water was applied from a rubber bulb through a hose and nozzle, but an integral system soon after was to apply a stream of water onto the cutting instrument.³ Many patented designs followed,^{23–38} some of which allowed compressed air to be applied to the cavity for debris removal. One even heated the air and water to minimize patient discomfort, and they could be released simultaneously. Alongside this, more effective aspiration was required.^{39,40} Hollow burs,

through which air is passed to supplement the cooling provided by air and water jets, were devised in 1974^{19,41} but failed to gain widespread use, despite a similar principle being used in surgical instruments.

The start of the modern turbine era may be 1941, when a patent claimed 25 000 rpm (417/s) for a design using compressed air at 45 psi (310 kPa).⁴² The turbine rotor was unusual: a cylinder with a circular arrangement of holes through which air jets from two nozzles were directed. In addition, ball bearings were to be used (as opposed to the sleeve bearings of earlier handpieces), and the inner ball race of the bearing at the chuck was arranged to cause the jaws to open and close by a sliding action, thus facilitating the rapid change of instruments.

The first demonstrations of Norlén's device in London, UK were in May 1958,⁴³ although it had been patented in 1952.⁴⁴ Turbine rotation was transmitted to the instrument via a mechanism in the body of the handpiece, which was interchangeable by a slip-joint connection. Multiple nozzles directed air onto inclined, slightly shovel-shaped turbine blades. Speed control was by means of adjusting the opening of vent holes. Said to reach a rotor speed of 120 000 rpm (2000/s), a ball-race reduction drive gave an instrument speed of 50 000 rpm (833/s). A finger-operated spring released a brake and progressively opened the air inlet.

There has been much debate over the history of the first handpiece with a turbine in the head (see below),^{43,45} a distinct advance in design first developed in New Zealand. Arising from the vibration studies mentioned above, as an adaptation of a commercial air-powered drill, it reached 60 000 rpm (1000/s), but was very noisy and exhausted excessive air into the patient's mouth. As no suitable bearings were available, overheating and seizure occurred after a short period of use.⁴⁶ The project was abandoned.

A water-driven, head-mounted turbine contra-angle handpiece was reported in 1953.⁴⁷ The small rotor (diameter, 7.5 mm; height, 4.8 mm) had six notched blades and could rotate at 61 000 rpm (1017/s). Hollow-shank cutting instruments were fitted directly to the rotor shaft, retained by a spring and keyway. Although referring to a number of earlier turbine designs,^{2-4,42,44} the New Zealand design seems to have been unknown to the authors.⁴⁸ Further development had a complicated history,^{43,45} but by 1956 it was being sold as both straight and contra-angle handpieces and could operate at up to 100 000 rpm (1667/s).⁷ The drive water was recirculated by coaxial tubing to the pump, and threaded rotary instruments were attached to the turbine shaft. This was said to be 'extremely quiet during operation' and to have 'the highest torque of any turbine angle handpiece'.⁷

Meanwhile, development of cord-driven equipment continued, although speed was limited by the difficulties of transmission. However, in 1951, a 10 000 rpm (167/s) device using an 'accelerating wrist joint' was produced.⁶

Then, in 1955, with the elimination of gears, the Page–Chayes handpiece reached 100 000 rpm (1667/s), relying on a cord and pulley system inside the handpiece sheath, and went on to reach 180 000 rpm (3000/s) by 1960.^{7,49} Although the definite benefits of high rotation rate were obtained, the cord arm mechanism remained cumbersome.

The most significant event in this history was the production in 1957 of the first commercially-viable high-speed air-turbine handpiece, the Borden Airtor. Said to be able to run at up to 300 000 rpm (5000/s) it had oil-mist bearing lubrication and an integral water jet for cooling.⁵⁰ It sold quickly: by 1958, it was claimed that 50 000 had been sold. Other manufacturers rapidly followed suit. In 1960, the Borden Airtor 60 was advertised as having the advantages of a smaller head, reduced noise, and an improved cooling system with twin jets. The greater convenience and manoeuvrability of the high-speed turbine handpieces led to their market dominance and the disappearance of cord systems.

Patented designs continued to appear, including finger-operated air and water coolant valves, and needle roller bearings for the rotor which acted as the turbine blades.⁵¹ The ball bearings initially used were noisy, required continuous oil-mist lubrication, and wore out rapidly.^{50,52,53} Air bearings, introduced in the early 1960s, permitted speeds up to 528 000 rpm (8800/s) to be achieved with air at 60 psi (415 kPa).^{50,52,54} Said to be quieter, but requiring a lower load during cutting than ball bearing devices because of the ease of stalling, such handpieces are still in production. Since the 1970s, however, improved, more durable ball races have been available,⁵⁰ needing only periodic oiling, and this design is still dominant. Ceramic bearings, said to require no lubrication, were introduced in 1991.

Low-speed work was still considered appropriate in some contexts, but cord systems remained problematic. The Dentatus air motor, introduced in 1960, could operate across a wide range of speeds with relatively high torque. This was in effect, a piston motor: plastic balls acted as pistons in an eccentric rotor. Several manufacturers produced similar devices, but all were ‘rather noisy’.⁵⁰

In the early 1960s, small high-torque 24 V dc electric servo-motors for use in aircraft became the model for a quiet alternative: so-called ‘micromotors’.⁵⁰ Air-drive vane motors – the rotor having radial slots containing sliding vanes, rotating in a non-circular casing – were also developed. Capable of 20 000 rpm (333/s) with ‘remarkably high torque’, the advantage was a simple air-driven control system, as have air-turbine handpieces. Both air motors and low-voltage electric motors continue to be used today.

Perhaps prompted by the great success of the Borden Airtor and its successors, there has been lively competition to attribute credit to various individuals.^{43,45} As it turns out, the idea of placing the turbine in the head of the handpiece appears to have occurred independently to two separate

groups and it is inappropriate, certainly invidious, to seek a single originator. Subsequent developments in high-speed air-turbine handpiece design are of two types: turbine modifications that affect speed and torque, and modifications affecting task suitability or convenience of use. Of these latter can be mentioned multiple coupling connectors with rotatable joints, fiberoptic illumination, push button and lever chuck systems, the ability of the handpiece to withstand routine autoclaving, and ceramic bearings. Larger diameter rotors give increased torque, while smaller rotors (both diameter and length) reduce handpiece head size and thus improve accessibility in the patient's mouth. Improved bearings require simplified lubrication and last longer, but there are no clear distinctions to be made between the many variations of rotor blade design.

1.4 Importance with respect to cutting: work done vs. power in, duty cycle, load, nature of substrate

Cutting performance is understood to relate to the rate of reduction of the workpiece. This is affected by many factors, for example operator characteristics, the handpiece itself, rotary cutting instrument design, coolant applied at the interface, and the workpiece material. Given this, it is not possible to define a representative set of conditions for 'normal' clinical service. Only benchmarking in certain respects, item by item, is presently feasible. A detailed discussion has been given elsewhere,⁵⁵ but an outline follows here to illustrate the nature of the problem. It will be understood that this must relate to all aspects of the system: powering device, cutting instrument, cooling, and substrate.

Speed

'Normal' use does not involve constant speed (as in many other systems) but rather an intermittent, continuously-varying rotation rate. As it is expected that the interaction between cutter and substrate depends in part on relative velocity (and thus the strain rate-sensitivity of the substrate), this 'duty cycle' needs to be studied and standardized, and probably with different conditions applying for different cutter-substrate combinations. Furthermore, the volume swept by a cutter blade is proportional to speed, so higher rotation rate means higher rate of removal, if other factors are held fixed.

Angle of attack

This refers primarily to the geometry of the relationship of the blade or cutting point to the surface of the substrate as it affects stresses, flow

patterns, and tool wear. However, the attitude and translational motion (i.e. the direction and magnitude of the guiding forces) of the rotating instrument as a whole affects the interface with the substrate, for example: area covered, cutting direction with respect to rotation axis, chip removal, and coolant path, as well as the loads acting on the bearings.

Depth of cut

Obviously, the length of the contact between cutter and substrate affects the volume swept by a blade or point, and thus the work required for cutting.

Cutting instrument design

Factors include: number of blades and their type, e.g. straight, spiral, interrupted; blade rake and clearance angles; sharpness and wear rate, i.e. material properties. Chip clearance affects behaviour: clogging effectively changes cutter design, as does wear, during the course of use.

Coolant

The properties of the substrate depend on temperature (as do those of the cutter), hence on heat transfer rates, via effectiveness of delivery and clearance of coolant. Mechanical properties also depend on the chemical environment provided by the coolant (zeta potential), hence the work of cutting is further affected. Temperature depends on heat delivery, which depends on friction and plastic work done, as well as thermal mass: volume and specific heat, and thermal diffusivity.

Substrate

Again, the mechanical properties of the substrate affect fracture work required, chip behaviour, and cutter wear. No one material can substitute for all possible dental substrates; standardization is therefore not possible.

Power

The rate of material removal depends on the delivery of the energy of fracture and deformation (as well as friction), and thus on the efficiency of the conversion of the drive power to cutting work, via cutter design etc. Even so, this is fundamentally limited by the maximum power that the device can deliver. For a given input, all work done reduces the speed.

Torque and speed

Turbine design, including all aspects that affect air flow to and from the device, determines unalterably the mechanical properties of the machine. Torque and speed are complementary: at maximum, free-running speed no external work can be done as there is no deliverable torque; at maximum torque the machine is stalled. Power is the product of the two, and the maximum occurs at the speed midpoint. The feedback between available torque and actual speed is critical.

Air pressure

As pressure affects flow and the potential for doing useful work, so variation of source pressure affects outcome. Hence, factors such as: connector design; tubing bore smoothness, internal edges and bends; local or remote exhaust; leakage and use as coolant are also involved.

Temperature

Gas behaviour depends on temperature and thus heat flow into the expanding air affects work done.

Bearing friction

Work done in turning the bearings is not available for cutting. Bearing design, conditions – size, design, wear, lubrication, alignment – therefore have a significant influence.

Load

Referring to the normal force of the cutter on the substrate, this affects how much material can be removed but also the forces in the bearings, and thus their friction. However, load is not constant, and the load cycle needs to be studied to ascertain a reasonable standardized pattern.

Substrate relationship

Unlike machine tools, handpieces are hand-held. There is no fixed geometrical relationship (cutting depth) or feed rate. Steady-state conditions cannot be attained.

Feedback

The user has auditory and tactile feedback during the course of cutting, depending on substrate material and cutter design. The interpretation and

effect of this must vary between operators, as well as expectations of hand-piece behaviour, and are also affected by intention, i.e. whether gross material removal or fine adjustments are required.

It is clear that there is much interaction between all of these factors. Furthermore, there are several significant impediments to full standardized testing: load and duty cycles are unknown, and suitable standardized substrates for tooth tissue are not available. Thus, while the primary concern is to understand actual cutting, it is clear that it is at present not possible to address this in any useful fashion. Accordingly, we are limited to characterizing the machine driving the cutter. It is these measurements and tests that are set out below.

1.5 Testing: equipment, procedure, calculations

Although it is the core of the device, the design requirements for the rotor are poorly understood. In common with many other developments in dentistry, there has been no theory to guide design. This is in contrast to that of large-scale industrial turbines, where a great deal is known. At the scale relevant here, there is little that can be said about which factors control which aspects of behaviour. Despite an extensive search, the characteristics of a wide variety of handpieces could not be explained in terms of the dimensions (other than diameter) of the rotor, the number of blades or their shape.⁵⁶ This is an area worthy of further study, as the variety of existing designs suggests that, like tyre treads, there is little to choose between them: they all work, indistinguishably. Other factors have greater importance. Nevertheless, devices vary. It has been found necessary to resort to the ‘black-box’ approach and determine the ‘pressure effectiveness’ of the unit. That said, air flow is clearly controlling and, therefore, details of the plumbing, nozzles and vents are important. Here, too, it is not possible to assign quantitative descriptions to these factors – a ‘black-box’ approach is again necessary. This results in the ‘equivalent orifice’ determination described below. Further information and background may be found in the authors’ publications.^{43,45,55–61}

The aspects of the performance of air-turbine handpieces of principal concern with respect to turbine performance are free-running speed (maximum rotation rate), that is, with no external load applied, and torque (and hence power) as functions of speed, rate of air flow, and supply pressure. However, since the bearings are the primary source of internal friction in most designs, a standardized lubrication protocol (and according to the manufacturer’s requirements) is an essential first step in any testing, at least for steel bearings. A self-contained test system has been designed to perform the most important tests.⁶¹

1.5.1 Pressure

Air pressure is the principal input variable, and sufficiently precise, high-quality pressure transducers are readily obtainable: with high accuracy and linearity, low hysteresis, and high repeatability. However, it should be recognized that the value of the pressure observed in a flowing gas is not directly usable in any calculations: there is a correction to be applied to obtain the so-called ‘stagnation pressure’, of the stationary gas. This can be done as described elsewhere.⁶⁰ Pressure needs to be measured as close as possible to the handpiece connector.

In order to control pressure a regulator is required in the supply line, but while manual types are acceptable, for any work that involves measurements at a series of pressures, a stepping motor-driven regulator allows both ready setting at fixed values and scanning when continuous recording is undertaken. The linearity of such regulators is, however, only approximate at best, and actual observed pressure (for subsequent conversion to stagnation pressure) should be recorded rather than controller setting; some variation will occur.

1.5.2 Flow

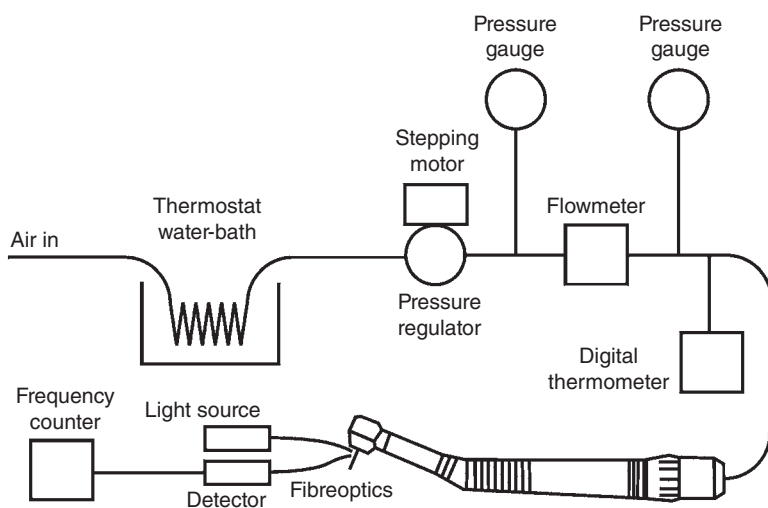
The accurate measurement of flow rate is a relatively difficult proposition. Temperature variation in the supply pipework, whether from location or the flow of the air (which entails expansion and thus cooling or heat absorption) needs to be carefully controlled. A thermostatted heat exchanger (a long coil of copper tubing in a water bath) close to the point of use has proved to be essential, as well as working in a closely temperature-controlled environment. No matter where the control mechanism is placed, pressure must be measured close to the handpiece (and downstream of the controller) because there is necessarily a pressure drop along any practical size of tubing for this work. This latter also means that, where possible, large-bore connections, without restrictions, are used. Of course, expansion of air through the pressure controller affects temperature, but in practical terms it is only necessary to ensure steady-state conditions and then record the relevant values. Too great a pressure reduction should, even so, be avoided, and the supply line should be arranged to be at a pressure only slightly above the maximum ever required (typically about 4 bar) and of sufficient bore that, when running at full capacity for the handpiece in test, the pressure drop to the regulator does not become a problem, as some do not have a completely independent output.

‘Rotameters’ are the most convenient device for measuring flow, but rarely can they be read visually to better than a few percent of full scale. A rotameter with an optical position-sensing mechanism is better and both

avoids reading errors and reduces the effect of the unavoidable noise in the float position. Devices good to $\pm 1\%$ full scale are available, but even so the absolute accuracy is likely to be inadequate for precise work and a calibration curve needs to be constructed. It is beyond the present scope to give full details of this, but it essentially requires: a direct measurement of the amount of air delivered, corrected to 1 bar, in a measured time (or time for a particular volume) at a large number of points in the range; a smoothing function to be applied which preserves the non-linearity and local anomalies of the device; and a look-up table being constructed to convert each discrete display value to an actual flow rate in equivalent terms at the standardized conditions of temperature and pressure. This must allow for the effect of varying density in the flowmeter (which affects the reading directly) due to the actual pressure in the flowmeter. Note must also be taken of the working altitude (barometric pressure), and corrections made appropriately – the handpiece behaviour is also affected by these variables.

The pressure drop across the rotameter requires that an additional pressure gauge, of identical type and specifications to that already fitted close to the handpiece connector, is installed in the line near the flowmeter's gas input (Fig. 1.1). The rotameter sees its supply pressure, the handpiece sees the pressure after that drop, hence the need to reduce the flow data to common, standard conditions.

In general, flow is unaffected by handpiece load (i.e. turbine speed) and, in most cases, it is essentially unaffected by stalling the rotor. In a few cases,



1.1 Outline diagram of the instrumentation for characterizing an air-turbine handpiece.

a small reduction (0.1–0.3 L/min) occurs in specific rotor positions (i.e. with a rotor blade adjacent to the supply nozzle, effectively blocking it), although slow rotation ($>1/s$) causes the effect to become undetectable and thus of no practical importance.

Connection of the air supply to the handpiece needs to be made via the appropriate three-hole or four-hole connector. In normal clinical use, four-hole connectors have flexible tubing attached to the exhaust port to carry the exhaust gas back to the dental unit. Variation in the resistance to exhaust flow is to be expected from this source, depending on the length, bore, and degree of bending of the tubing. It is a matter for consideration whether this effect is to be included or avoided. No attached tubing is preferred for handpiece characterization. Typically, three-hole connectors have apertures for the exhaust air, and these must be left unobstructed. It is worthwhile checking that the entire system up to the handpiece itself is leak tested. Pressurizing to 4 or 5 bar, say, and shutting off the air supply at source, allows observation of any pressure drop with time. Less than, say, 0.05 bar in 2 min may be considered adequate.

Since the purpose is generally to measure flow through the turbine alone, it is necessary to block any coolant nozzles that use air, or by closing the supply tube at the handpiece connector. Otherwise, no attempt should be made to close any leaks around the handpiece head as these are properly part of the actual working design. Any internal flow restricting mechanism in the handpiece (to allow a switch to be made between two alternative supply pressures at the connector) should be noted, but most commonly these are set in the open position in practice.

The complexity of the gas path in the handpiece means that no simple theoretical equation exists to relate actual flow rate, $\dot{V}$, after the necessary corrections, to the supply (absolute) stagnation pressure, p_0 , and at that pressure. The pragmatic ‘black-box’ approach entails a simple non-linear curve fit. The following function provides an adequate description of the behaviour:

$$\dot{V} = \dot{V}_L \left[1 - \left(\frac{A}{p_0} \right)^b \right]^{1/2}$$

A and b are the parameters to be fitted and which control the curve shape (A represents ambient pressure, but b cannot be interpreted in terms of a specific feature of handpiece design), and $\dot{V}_L$ is the limiting flow rate (i.e. at ‘choke’) which corresponds to the flow at some point in the system reaching the sonic velocity. Since such a condition can occur even in a simple circular orifice (such as the nozzle in the turbine head), the handpiece can be characterized as being equivalent to such an orifice via the equation for choke. The relationship is:

$$\dot{V}_L = \pi r_e^2 c$$

where r_e is the effective radius of that orifice and c is the speed of sound, itself given by:

$$c = \sqrt{\frac{\gamma p_0}{\rho}}$$

where ρ is the density under the prevailing conditions, p_0 is the absolute stagnation pressure, and γ is the ratio of specific heats c_p/c_v (which may be treated as a constant as the absolute temperature is sufficiently high and changes are moderate). The area of the equivalent orifice, πr_e^2 , is therefore a measure of the ability of the handpiece to deliver air to the turbine in a strictly controlling sense.

If the flow rate needs to be expressed in terms of ‘free air’, i.e., at atmospheric pressure, to relate this to compressor pumping capacity, for example, the isothermal gas law (Boyle’s) is used:

$$V_2 = p_1 V_1 / p_2$$

where p_1 , p_2 are the pressures and V_1 , V_2 the volumes before and after expansion to atmospheric pressure, respectively.

1.5.3 Temperature

Supply air temperature can be measured well enough with a type-K thermocouple placed in the gas flow beyond the flowmeter, providing this does not interfere with the flow, i.e. it is small enough. A T-piece such that the thermocouple is level with the supply line wall is adequate. However, it must be remembered that all gas calculations are in terms of absolute temperature.

1.5.4 Speed

Many methods have been used to monitor rotation, with varying degrees of success. These techniques have been reviewed in detail elsewhere,⁵⁸ and the deficiencies identified. Clearly, any technique that requires work from the rotating system is unacceptable, and non-contact methods are essential. Likewise, anything that appreciably changes the angular inertia or balance of the system is inappropriate. Severe errors are introduced if these points are not adhered to. The most effective means of speed monitoring is optical, and a fibreoptic tachometer can be used to measure the rotational speed of any handpiece, cutting instrument, or test mandrel; it provides no load on the turbine and has minimal bulk. Ultimately, such an approach would be intrinsically safe for patient contact.

A sheathed 1-mm-diameter acrylic optical fibre with polished ends can be used to transmit light from a (heat-filtered) quartz halogen lamp onto the shaft of the tool in the handpiece chuck. The shaft needs to have approximately one-half of its circumference close to the nose of the chuck coated with a matt black ink (i.e. of very small mass), the remainder being left bright. A second optical fibre, similar to the first and at right angles to it, is then held in a position to receive light reflected from the unpainted half of the shaft such that at each rotation the receiving fibre returns a pulse of light. This is then to be applied to a photo-detector whose output is connected to a frequency counter. This latter needs to be of high stability and with no zero-offset,⁶² but with a recordable output signal proportional to frequency, and hence speed. Alignment of the optical fibres is best done using an oscilloscope to view the signal, using auto-triggered time-sweep mode. Adjustment should be aimed at obtaining an approximately 50% on-off (duty) cycle.

1.5.5 Free-running speed

The mandrel with the half-black sector is fixed in the handpiece chuck and the optical fibres adjusted and checked for correct operation (oscilloscope). If a pressure scan is undertaken, the rate of pressure change needs to be slow in relation to the response time constant of the system as a whole (equilibration of the gas stream, inertia of the turbine assembly); this can be determined by trial and error, but probably no more than about 1 or 1.5 bar/min is appropriate. The maximum pressure used depends on the equipment used, but clearly it needs to be checked for safety. Even so, 4 bar probably represents a general upper limit, depending on the relevant manufacturer's recommendations. A double cycle of raising and then lowering the pressure to zero allows a check of reproducibility. Supply pressure, temperature, and rotation rate are logged.

The upper limit to the rotational speed attainable for a rotor is set by the speed of sound, so the actual free-running speed N_f is expressed through the peripheral Mach number Ma^* at a given supply pressure:

$$Ma^* = 2\pi r_f N_f / c$$

where r_f is the radius of the rotor. There remain turbine behavioural variables that have yet to be resolved, as indicated above, so the 'black-box' approach is used to define a rotor performance coefficient, α_r :

$$\alpha_r = \frac{\{1 - (\gamma - 1)(Ma^*)^2\}^{-\frac{\gamma}{\gamma-1}} - 1}{\pi r_e^2 p_{0g}}$$

which takes into account all such remaining aspects, determined from the free-running speed and absolute stagnation pressure of the air supply,

through the equivalent orifice. Note the subscript ‘g’; this is a gauge pressure, i.e. the difference between the actual absolute stagnation pressure and the surrounding atmospheric pressure. However, as far as the user is concerned, it is how well the device utilizes or translates the supply pressure. Hence, we may combine the effective orifice and the rotor performance coefficient into a single descriptor, the ‘pressure effectiveness’, α :

$$\alpha = \alpha_r \pi r_c^2 = \left[\{1 - (\gamma - 1)(Ma^*)^2\}^{-\frac{\gamma}{\gamma-1}} - 1 \right] / p_{0g}$$

This can be determined as the slope of the least upper bound of a plot of the square-bracketed term on the right vs. p_{0g} . Numerically, free-running speed can then be estimated from

$$\hat{N}_f = \frac{5.0358}{r} \sqrt{T \{1 - (1 + \alpha p_{0g}/p_{at})^{-0.2867}\}}$$

where p_{at} is the (absolute) atmospheric pressure in bar, and T is the absolute temperature of the supply air.

1.5.6 Torque

Torque (τ) is defined as the moment of the force that tends to produce rotation. From Newton’s third law of motion, this force is equal and opposite to the shaft braking force:

$$\tau = Fr$$

where F is the braking force and r is the radial distance of the point of application of that force from the axis of rotation. If the braking force is gradually increased from zero, the turbine speed will progressively reduce until it stalls. Thus, for a given turbine, τ vs. rotation rate (N/Hz) can be plotted, the maximum value for τ being at the point of stall.

Braking force is most easily determined by the technique known as a ‘rope brake’.⁶³ This requires a thread wrapped around the rotating shaft, friction being applied by tension in that thread, the braking force. The measurement is best performed with a load cell on a universal mechanical testing machine, or equivalent frame, for stability and accuracy. The shaft or drum in contact with the thread needs to be rather well-polished if excessive wear (and frequent replacement) of the thread is to be avoided in dynamic torque tests. Even so, replacement can be expected to be required when oxidation becomes excessive and polishing no longer practical. The shaft can become quite hot and it is important to allow it to cool between runs if the thread is not to burn. While in principle almost any kind of thread will suffice, in practice there are some factors to be borne in mind. The heat

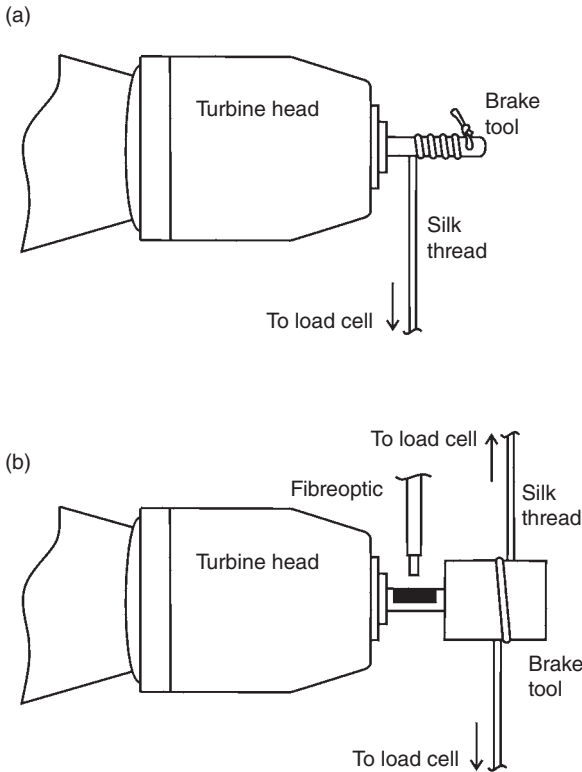
of friction may melt thermoplastic polymers, and stable close approximation of thread to shaft is essential for steady values to be obtained. The latter implies flexibility, as obtained from a fine-fibre yarn. Similarly, a yarn that tends to flatten somewhat and obtain more points of contact will be preferable. Overall, the most effective thread has been found to be braided suture silk. Lubricants are of no benefit in this context. Displacement over time causes erratic effects, and their stickiness can cause the fibres of the thread to catch and bind.

The effective end of the moment arm does not lie at the surface of the drum or shaft in contact with the thread, and a small error will be present if this is assumed. For the braided suture silk that is recommended for the thread, the correction amounts to one-third of the thickness when flattened under load. This is measured well enough by a caliper gauge on the overall diameter with the thread in place.

A universal mechanical testing machine fitted with two load cell amplifiers (LCAs) and two load cells (10N full scale range is appropriate) can be used to measure forces and thus deduce torque. One load cell is mounted (say) on the upper, fixed, crosshead and the other to the upper surface of the moveable crosshead, ensuring the two load axes are accurately aligned. A self-centering thread attachment is required on each. Provision for clamping the handpiece accurately in place must be made so that its position with respect to the load axis is preserved, most conveniently this is fixed to a crosshead (a hard rubber 'V-block' mounting is satisfactory, but see reference 61 for a more precise approach).

1.5.7 Bearing resistance

This is the torque required to rotate the turbine against the friction of the bearings. Note that this cannot be done for air bearings (which one hopes would have negligible intrinsic friction) as they require air to be supplied in order to operate. A brake tool can be prepared from a highly polished mandrel, of accurately measured diameter, by drilling a small (say, 0.70 mm) diameter hole perpendicular to its axis and 1.5 mm from one end (Fig. 1.2a). The tool being fitted in the handpiece chuck, the handpiece is then placed in the mounting. Alignment of the brake tool is critical. A datum can be provided by attaching a (silk) thread to the upper and lower load cells, and placing this under slight tension. The handpiece position can then be adjusted so that the surface of the brake tool just contacts the thread, some 2–3 mm from the drilled hole. An engineer's parallel can be used as a horizontal datum for the axis of the brake tool with respect to the frame of the testing machine and thus normal to the thread. The handpiece must then be firmly clamped and the thread between the load cells can be removed.



1.2 *a* Design and use of brake tool for determining bearing resistance, *b* design and use of brake tool for determining dynamic torque.

A 150mm length of silk thread is then passed through the hole in the mandrel and secured with a knot, and the other end is attached to the thread holder of the (movable) load cell by means of a loop tied at its free end. The moving crosshead is then moved to apply a slight tension to the thread ($\sim 1\text{ N}$), and air at a pressure of $\sim 1\text{ bar}$ is supplied to the handpiece while the crosshead is slowly moved ($\sim 10\text{ mm/min}$) so that the thread can be guided manually to wrap around the braking tool with four to five slightly-spaced turns (they must not overlap), driven by the turbine.

The air supply is then removed and the crosshead set to move at (say) 5 mm/min so that the the force can be recorded for at least one full revolution of the turbine. Rotational position needs to be noted carefully for this. The bearing resistance (as torque) is then calculated as the mean for one full rotation.

1.5.8 Stall torque

This is the torque generated by the air flowing through the non-rotating turbine. The same set-up is used as for bearing resistance (Section 1.5.7), but now the air pressure is adjusted to that required for the test, allowing a few seconds for stabilization. The moving crosshead can then be moved away at, say, 5 mm/min for recordings to be made of pressure vs. load and flow rate until the turbine has rotated through at least 360°. For repeat tests, or tests at other pressures, the crosshead is returned to its original position while the thread is guided back into evenly spaced turns on the tool as above. The rate of crosshead movement chosen must be slow enough to effectively stall the turbine. No distinction can then be made between the values obtained with this rate of movement and those achieved by stopping the crosshead at frequent small increments. Stall torque is then taken as the average over a full rotation, as determined by reference to the variation (if any) with position and a knowledge of the number of blades and nozzles in the device. Such recordings also allow the effect of rotor position to be investigated. It is to be noted that averaged stall torque is not, in general, the same as the mean of the upper and lower limits observed: the variation with rotor position is more complicated than permits this simple calculation. In effect, it is determined by the area under the curve for one full rotation, a properly weighted mean over all positions.

Stall torque is directly proportional to the stagnation air pressure, p_{0g} :

$$\tau_p = \Phi p_{0g}$$

where Φ is the stall torque coefficient, atmospheric pressure of 1 bar. Thus, in principle, only one determination needs to be made in order to predict behaviour at other pressures, providing the air flow remains subsonic (which is the case in the dental context).

1.5.9 Dynamic torque

Although the theoretical torque behaviour of a driven rotating system is well-understood, the effects of imbalance in rotor or tools can only be detected dynamically. Thus, a direct measurement of dynamic torque may be of value as a means of detecting imbalance or resonance which can only reduce the available torque.

Brake tools, with highly polished drums, may be made by precise machining from stainless steel. Because the balance of the brake tool is crucial to this test, those to be used must first be screened using a hand-piece that has been shown by trial to be well-balanced and to show no resonance effects itself. A free-running speed vs. air pressure scan then allows those tools with defects to be discarded. This is a very severe test,

but a discrepancy of more than 300/s at any pressure can be taken as a convenient criterion for discard. If the brake tool drum diameter is too small, the thread tends to break before stall can be achieved; too large and obtaining satisfactory balance becomes too difficult. Some 3.0 ± 0.5 mm may be suitable.

The diameter of the brake drum needs to be determined accurately with a micrometer screw gauge or equivalent device (and corrected for thread thickness as described for stall torque) before being fitted in the handpiece chuck. The handpiece is then mounted and aligned as for stall torque. A check should be made that the speed detector is working properly and the load cells zeroed and calibrated, confirming by applying a slight tension to the thread (-2 N) that the outputs are equal. However, it is the difference in load that is required for the actual test and this may be obtained directly by a differential voltage recording, or by post-processing of the two load signals.

The movable crosshead is then moved (no air pressure applied to the handpiece) to allow a single turn of the thread to be passed over the circumference of the brake drum (Fig. 1.2b). The crosshead is then repositioned to tighten the thread sufficiently to prevent rotation of the turbine at the maximum supply pressure to be tested. (Differential) force vs. speed can then be recorded while the crosshead is raised and lowered, at 1 mm/min between the points giving (close to) the free-running speed (with zero difference signal from the load cells) and stall. It should be noted that the slightest touch of the thread is enough to slow the turbine, and the true free-running speed will not be reached in this test. Resonance effects can lead to marked (negative) deviations of the torque-speed plot from the expected straight line.

The supply pressure required to start a turbine may vary according to the position of the rotor at stall. It is therefore easiest to determine the stall pressure or torque only on lowering the pressure, although the direct measurement of stall torque as described above is a simpler procedure.

The expected torque at any supply pressure, $\hat{\tau}_p$, is expressed by the following equation:

$$\hat{\tau}_p = \Phi p_{0g} \left(1 - \frac{N}{\hat{N}_{fp}} \right)$$

That is, it decreases linearly with speed N to zero at the free-running speed, $\hat{N}_{fp}$, simply scaling the stall torque by the proportion of the free-running speed then exhibited. (The subscript 'p' is added to the free-running speed symbol to emphasize that it is pressure-dependent and specified for the stated supply pressure, p_{0g}).

1.5.10 Power

The rate at which a handpiece supplies energy to the cutting site, its power, is determined by the handpiece's torque and speed. These describe the ability to carry out cutting work but such data will be essential for use in the analysis of cutting behaviour, when this becomes feasible.

Power (P), the rate of doing work, is given by:

$$P = \omega\tau$$

where ω is the angular velocity in radians/s

$$\omega = 2\pi N$$

i.e.

$$P = 2\pi N\tau$$

Determination of power thus, in principle, requires (dynamic) torque and rotation rate to be determined simultaneously. We can, however, write for the expected power, $\hat{P}$:

$$\hat{P} = 2\pi\Phi p_{0g} \left(1 - \frac{N}{\hat{N}_{fp}}\right) N$$

which is therefore a parabolic curve with zeros at stall and free-running. The maximum expected power, $\hat{P}_{max}$, therefore occurs at half the free-running speed, $N = \hat{N}_{fp}/2$:

$$\hat{P}_{max} = \frac{\pi}{2} \Phi p_{0g} \hat{N}_{fp}$$

1.5.11 Efficiency

There are several possible approaches to the definition of efficiency in the present context, but the primary interest may be in the demands placed by the handpiece on the compressor. Thus, we take the efficiency of a handpiece as the ratio of the useful work done at the rotary cutting instrument to the potential work in the supplied compressed air. Actual power is obtained from torque and speed as above, while the potential energy of the air supply is the maximum work available when the air expands to atmospheric pressure. Here, we may reasonably assume that the air behaves sufficiently like an ideal gas. As the expansion occurs quite rapidly it may further be assumed (conservatively) that this process is adiabatic and reversible (i.e. non-dissipative). The maximum work available on expansion (W) for a given flow rate $\dot{V}$ m³/s (at the supply pressure) is given by:

$$W = \frac{\dot{V}}{1-\gamma} (p_1^{1/\gamma} p_2^{(\gamma-1)/\gamma} - p_1)$$

where p_1 and p_2 (in Pa) are the inlet and outlet absolute stagnation pressures, respectively. Efficiency (η) is then given by:

$$\eta = \frac{P}{W}$$

The difference between P and W depends on the rate at which ‘unused’ energy is discharged in the exhaust plus the total rate of energy loss due to friction in rotor bearings, air flow within the handpiece, and noise emission (which is in fact small). It may therefore be seen that handpiece efficiency (η) at any particular speed (N) may be determined from measurements of supply pressure (p_1), air flow (V_1/s), and torque (T). The maximum efficiency is seen to occur at the maximum expected power:

$$\eta_{\max} = \frac{\hat{P}_{\max}}{W}$$

1.5.12 Longevity

The working life of a dental air turbine is limited by the length of time its bearings can adequately function under the conditions imposed during clinical work. Standardized laboratory longevity tests of the rotor-bearing assembly require that the handpiece is subjected to the same patterns of use that might be expected in clinical practice, that is, in respect of duty cycle, axial and lateral loading, lubrication state, and cleaning and sterilization procedures. This is very time consuming and laborious. Only one report of a study involving this kind of work has been published.⁶⁴ Bearing longevity tests in which only gross failure (such as collapse of bearing casings or seizure) can be detected require the handpieces to be run for lengthy periods, but, in view of the ordinary expectation of lubrication for metal bearings, such results may not be very meaningful. However, bearing resistance may be monitored as a sensitive means of detecting wear or corrosion. Acceptability criteria have not been established in this sense.

1.5.13 Comparisons

Given the sensitivity of several of the above measures to the supply pressure, it is clearly not easy to make comparisons between devices whose recommended pressures differ, except in a restricted sense. Indeed, a manufacturer could raise the torque and power of a handpiece simply by specifying a higher working pressure. It is therefore informative to use standardized

measures at an arbitrary but representative supply pressure, say, 2 bar. We can then define the following:

- standardized free-running speed

$$N_{I2}$$

- standardized power index

$$PI_2 = \pi \Phi \hat{N}_{I2}$$

- standardized efficiency index

$$EI_2 = \frac{PI_2}{W}$$

- standardized air consumption

$$p \dot{V}_2 = 3 \dot{V}_L \left[1 - \left(\frac{1}{3} \right)^b \right]^{1/2}$$

(where $p_{0g} = 2$, so $p_0 = 3$, and A is set to 1 bar in the equation on page 12)

It might also be convenient to determine the corresponding values for the recommended supply pressure, when this differs.

1.5.14 Figures of merit

Table 1.1 summarizes the descriptors and performance measures detailed in the above sections. The table is divided into two parts, the first containing

Table 1.1 Summary of the descriptive parameters and performance figures of merit for handpiece air-turbine behaviour

Character of factor	Symbol
Values required in the course of testing	
Turbine rotor radius	r
Limiting air flow	$\dot{V}_L$
Flow exponent	b
Equivalent orifice radius	r_e
Standardized free-running speed (2 bar)	N_{I2}
Rotor performance coefficient	α_r
Figures of merit of interest to the user	
Handpiece pressure effectiveness	α
Weighted mean stall torque coefficient	Φ
Standardized free air consumption (2 bar)	$p \dot{V}_2$
Standardized power index (2 bar)	PI_2
Standardized efficiency index (2 bar)	EI_2

those items that need to be determined for the testing itself, and the second those figures of merit that convey quantities that are directly comparable between devices and which are therefore of interest to the user. Some examples of values can be found elsewhere.⁵⁶

1.6 Hazards

There is a vast literature dealing with the hazards posed to the patient and dental personnel by air-turbine handpiece use. It is only possible to give a brief account here of the problems of heat, airborne materials, sterility, noise, projectiles and surgical emphysema.

1.6.1 Heat

Heat generation has possible harmful effects on the dental pulp, dental hard tissues and restorative materials. Temperature changes occur because of the thermalization of the work of friction and plastic deformation occurring at the cutter–substrate interface. Actual temperature depends on rate of power deposition and the thermal diffusivity of the materials involved, including the effects of coolants. However, care must be taken to distinguish purely thermal effects on vital teeth^{65–67} from damage that occurs due to mechanical vibration,^{68,69} dehydration,^{67,70–72} and the chemical effects of solutions or restorative materials that are subsequently applied.⁷³

Effects range from internal resorption⁷⁴ to dentinal reddening or ‘blushing’ due to dilatation and rupture of blood vessels, and extravasation of erythrocytes.⁷⁵ Histological changes include an inflammatory response (e.g. vasodilatation, haemorrhage, oedema, and infiltration of polymorphonuclear leucocytes),⁷⁶ changes in the layer of odontoblasts (e.g. the appearance of vacuoles within the layer,⁷⁶ and displacement of odontoblastic nuclei with separation from their cytoplasmic processes).⁷⁷ Some practitioners prefer to perform cavity preparation dry on the grounds that visibility is improved^{78,79} but there is much evidence that this is hazardous to the pulp.^{72,78–90} Air coolant alone is inadequate.⁹¹

Surface effects – such as smearing, cratering, and crack formation – that may occur during preparation of cavities and finishing of restorations have been observed,^{78,79,92–102} while dry cutting of enamel can induce sufficiently high thermal stress to fracture it,¹⁰¹ possibly aided by cracks induced by the hammering of blades. Raising the temperature of amalgam may melt it peritectically, while polymer-based materials may be raised above their glass-transition temperatures and suffer permanent plastic deformation or decomposition. Glass-ionomer and similar cements may be dehydrated.

1.6.2 Airborne materials

Material may be dispersed through the air as an aerosol or vapour when an air-turbine handpiece is used. An aerosol is a dispersion of solid or liquid particles in a gas, and may contain micro-organisms, oil, or particles of solid materials. Particles of all cut materials may be thrown up – including enamel, dentine, cement, and restorative materials – but also from the cutter: steel, tungsten carbide, diamond, and others.

Although such particles are generated by polishing lathes, air-abrasive prophylaxis equipment, ultrasonic scalers, and air–water syringes, air-turbine handpieces are among the most prolific producers of aerosols.¹⁰³ About 95% of the particles in dental aerosols have a diameter of less than $5\mu\text{m}$ ^{104,105} and may be fully inhaled.^{103–144} Larger particles may be carried considerable distances as ‘splatter’, when they are said to be ballistic,¹²³ and be deposited on exposed surfaces in the dental surgery, including the clothing and skin of the dentist and assistant, and into their eyes, noses, and mouths. Aerosols may be carried to other rooms.¹⁰⁵

Pathogenic micro-organisms of many kinds may be dispersed from the patient’s saliva or other oral fluid, carious dental hard tissues and infected calculus,¹¹⁷ the water supply to the handpiece coolant nozzle (either from the water source, reservoirs and tubing or from the patient by fluid retraction),^{129,138,145–150} and contaminated surfaces of the handpiece or rotary cutting instrument from use on a previous patient.¹⁵¹

1.6.3 Oil

Although continuous oil-mist lubrication is no longer required, bearing lubricants will be expelled in ordinary use for a considerable period. This may be inhaled, but oil contamination of surfaces for bonding procedures may be detrimental.¹⁵² Oil-free compressors are important for the same reasons.

1.6.4 Mercury vapour

Cutting amalgam generates mercury vapour as the peritectic melting of the γ_1 phase occurs at the relatively low temperature of about 70°C and this is easily attained under a cutting point. Water spray mitigates this considerably.^{140,153,154}

1.6.5 Airborne materials precautions

A number of precautions should be taken when using the air-turbine handpiece to avoid airborne material hazards:

- Water coolant should be used to reduce solid aerosols, mercury vapour,¹⁵⁵ as well as heat. However, this may result in an increased number of bacteria being disseminated in aerosols,^{108,120} additional measures are necessary.
- High-velocity evacuation can capture large volumes of aerosol.
- Rubber dam isolates the operating site from oral fluids.
- Good ventilation of the surgery will maintain low ambient concentrations.
- Face masks,^{119,121,128} transparent shields,^{118,156} protective spectacles,¹¹⁹ rubber gloves,^{157,158} and appropriate protective clothing¹³⁰ will protect dental personnel.
- Patient oral hygiene affects one source of bacteria.^{110,111,127,128,131}
- The dental unit water line should be properly maintained, regularly flushed,¹⁴⁸ treated, and filtered.
- Surfaces exposed to aerosol and splatter should be cleaned and disinfected.¹⁵⁹
- Lubricate handpieces with non-toxic oils.^{107,113}

It may be advisable to avoid the use of an air-turbine handpiece (or other device that produces profuse aerosols) when treating patients who are known carriers of communicable diseases such as hepatitis B,^{157,160} tuberculosis,^{109,126} or AIDS,¹⁶¹ although, with respect to hepatitis B at least, it has been pointed out that aerosols are ‘an uncommon and inefficient method’¹⁶² of transmission. Carriers of such infections cannot always be identified.^{163,164}

1.6.6 Sterility

It is now generally accepted that handpieces ought to be sterilized between patients. Surface disinfection by chemical agents¹⁶⁵ or ultraviolet light are inadequate. Older devices, however, may suffer destruction of plastic and rubber parts, and corrosion (especially of aluminium alloys) on autoclaving. Treatment dry may exacerbate this. Most current models appear capable of withstanding many cycles of steam autoclaving, but instrument changing tools, and the instruments themselves, should not be overlooked; nor should lubrication equipment and other objects that come into contact. Corrosion of bearings may affect performance.

1.6.7 Noise

The noise of air turbines, particularly the siren whine, may have several effects: auditory, psychological, sociological, and physiological. There may be some hearing loss in susceptible individuals, often temporary but

potentially permanent. It interferes with speech communication and the perception of other auditory signals. It is a source of annoyance and interferes with the performance of detailed or complicated tasks as well as adversely influencing mood. The repetitive exposure of dental personnel may increase the risk and severity of effects, but there is no evidence of a general problem.¹⁶⁶

Noise may be aerodynamic, that is, generated by turbulence in the gas flow, or structural, from moving parts such as bearings. Noise from the cutter is also present. Smooth air line design can reduce turbulence noise, but while silencers on the exhaust can be effective, they may restrict air flow and change the behaviour of the device, and, if adding weight to the device, would affect fatigue and precision of use. Four-hole as opposed to three-hole connectors may be preferable, again with the caveat about air-flow resistance.

1.6.8 Projectiles

The fracture of teeth, restorations, or indeed the cutting instrument, may result in a high-velocity projectile that is a risk to soft tissue through penetrating wounds, in the mouth or externally, to all present.^{167–169} Inhalation or swallowing of such fragments is also a concern. Attempting to straighten bent cutters may exacerbate the risk of fracture; proper balance is unlikely to be attained. Wear of the cutter may also lead to fracture.

1.6.9 Surgical emphysema

Surgical emphysema refers to the ingress of air into soft tissue as a result of injury or surgical operation. This may be caused if there is a breach in the oral epithelium, or when a tooth is opened for endodontic treatment, and any equipment is used that exhausts compressed air into the mouth. Air-turbine handpieces have been recommended in a number of contexts where there would seem to be a particularly high risk of this, and there have been many such reports:^{170–194} including pneumoparotid,¹⁹⁵ subcutaneous facial and cervical, mediastinal, and orbital. There may be grave or fatal complications: dogs may die if air is introduced under pressure into the root canals of their teeth, and indeed several people are thought to have died in similar circumstances.

1.7 Factors in selection and operation

It will be apparent from the above that we are as yet far from a complete characterization of handpieces that would enable clearly informed selection by the user. This is not helped by the fact that performance depends in part

on other factors, primarily cutter and substrate. Thus, definitive guidelines cannot be given, and only some general points can be made, more by way of food for thought than advice:

- There is a lack of satisfactory standards (the International Organization for Standardization (ISO), for example, has limited requirements).
- There is a lack of detailed specifications of performance provided by most manufacturers – although the use of simple figures of merit given here would allow comparisons.
- Ability to be autoclaved repeatedly is essential.
- Other less-commonly considered factors are also of interest: air consumption, ergonomics, noise, efficiency of coolant delivery.
- However, the buyer is often guided by the reputation of the manufacturer, appearance, price, and prior use.

In operation:

- Avoid use in procedures that involve (or may create) a breach in the oral mucosa; not for surgical or endodontic use; should also avoid use deep in the gingival sulcus (surgical emphysema).
- Ensure that the rotary cutting instrument is undamaged (imbalance leads to substantial vibration).
- Ensure that the lubrication routine is properly executed.
- Ensure that the chuck mechanism is operating correctly (risk of projectiles).
- After cutting, degrease the operating site before bonding (continuing oil discharge).
- High-volume aspiration (and rubber dam whenever appropriate) to reduce aerosol dispersion (infection control concerns).

In summary, in spite of some known concerns about its safety and operating convenience, the air-turbine handpiece remains as standard equipment for most dental cutting work. Research is needed to address the issues of:

- air and oil discharge into the mouth;
- optimal rotary cutting instrument design and handpiece operation;
- bearing longevity;
- noise and vibration;
- agreement between manufacturers on standards for describing their products would allow buyers to make informed decisions when selecting handpieces.

1.8 Future trends

Even with the movement towards minimalized preparation of teeth for restoration (e.g. ‘minimally invasive dentistry’¹⁹⁶ and ‘microdentistry’¹⁹⁷),

there will remain a need for cutting methods that can cope with the sectioning and removal of old restorations and bulk removal of tooth tissue for the provision of extracoronary restorations. Non-rotary removal techniques such as air abrasion and laser tooth preparation are employed for certain procedures that require minimal removal of material, but these are not appropriate for use on toxic heavy metals. However, most cutting work is still carried out using turbine handpieces or, in some cases, using electric motors and speed-increasing handpieces (gearing ratio 1:4 or 1:5, speeds 80000rpm or above). Such speed-increasing handpieces depend on the transmission of rotations through the handpiece body and head and are subject to wear of the components of the transmission system. There are arguments for and against electric devices.¹⁹⁸ Even so, future developments of both turbine and speed-increasing handpieces will depend on the availability of components such as bearings that will have lower maintenance requirements and improved longevity. Given that the designs of dental air turbines have changed little since they were first commercially introduced, and that manufacturers do not appear to be taking a systematic approach to development, it seems unlikely that any radically different turbine design, or indeed more efficient devices, will emerge in the foreseeable future. This is an economic constraint: it is not worth investing in detailed development when the product appears to work satisfactorily. However, the possibility of further improvement and acceptance of ceramic bearings, which will require neither lubrication nor corrosion protection, displacing steel bearings, offers the prospect of simpler maintenance, better adherence to the sterilization imperative, and removal of a source of oil contamination of prepared surfaces.

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Optical imaging techniques for dental biomaterials interfaces

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2.1 Introduction

With the naked eye it is practically impossible to detect structural failures within restorative materials and tooth tissue until these have become quite gross. Not surprisingly, microscopic techniques are therefore of great benefit for the *in vitro* and *in vivo* assessment of these failures. Such techniques can also be used to study the interactions between materials and the substrates to which they are applied, such as enamel and dentine.

All microscopic techniques will involve the interaction of the sample under examination with the interrogating system being used to probe it. Consequently, the ability to discriminate features within or upon a substrate will partly depend upon the wavelength, or spot size, of the interrogating system being used. As an example, electrons, possessing smaller size and higher energies, should enable better resolution of features than photons. However, there have been many developments over the last 130 years following Ernst Abbé's (1840–1905) determination of the resolution limit of an optical microscope. It is thus possible to use these systems in a variety of ways, to achieve the greatest level of resolution attainable, so giving important information about the structure and composition of materials interfaces. Unfortunately, there is also a risk that microscopists can become so engrossed in one small area that the macroscopic perspective is lost. Spanning the range from clinical observation to ultrastructural morphology is beyond the scope of most microscopic techniques.

Light microscopic techniques can be used at very low magnification, such as used by a clinician with an operating microscope, to much higher magnifications and resolution using techniques where the resolution of the microscope images is no longer limited by the wavelength of the light, as postulated by Abbé. Such techniques use sub-picosecond pulsed laser excitation to cause fluorescence emission of a dye molecule; this is then surrounded by an almost simultaneous longer wavelength quenching pulse that absorbs most of the fluorescence from around the dye molecule, so

tuning the fluorescence emission to an incredibly small point source; this technique is called ‘stimulated emission depletion’ or STED. Using this technique, Hell has achieved resolutions of 20nm, i.e. 10 times over the Abbé limit (Klar *et al.* 2000). It may be a while before such methods are widely applicable to biomaterials research, but such work indicates the potential of optical imaging techniques.

Imaging alone is not the only aspect that should be considered for optical techniques. Techniques such as fluorescence lifetime imaging (FLIM) measurements can give significant information regarding the interactions between biomaterials and their substrates and will be discussed later. Other optical techniques, e.g. Raman spectroscopy, will not be discussed here but there is an extensive literature reporting its use in biomaterials research (e.g. Wang *et al.* 2006). Raman instruments can also be used to generate images, but it is common to find that a method of image contrast and resolution improvement that has been established in the dental field for over 20 years will probably also be used in conjunction with these techniques. That method is confocal microscopy (Watson and Boyde 1987a,b,c). It is a technique that can be used both in the clinic and in the high-resolution microscopy suite. Instruments have been designed for use that are capable of intra-oral imaging as well as resolving features, such as lateral dentinal tubules, at sub-micron size.

2.2 Confocal microscopy

As with many imaging techniques in optical microscopy, the main function of a confocal imaging system is to improve image contrast: to delineate structures that would otherwise be difficult to see. The expression ‘confocal’ derives from the use of an aperture in the conjugate focal plane of an objective lens, in both the illuminating and imaging pathways of a microscope. The area surrounding the aperture rejects stray light returning from areas that are not in the focal plane of the lens. In order to see more than one small patch of the sample some form of scanning device is required. This type of scanning optical microscopy enables high-resolution images to be made of samples, often below the surface of translucent materials, with minimum requirements for specimen preparation.

High-resolution confocal microscopic images may derive from either the surface of a sample or beneath the surface. These images are thin ($>0.35\mu\text{m}$) optical slices up to $200\mu\text{m}$ below the surface of a transparent tissue. With microscopes running under ‘normal’ conditions, the optical section thickness will be $>1\mu\text{m}$ and the effective penetration into enamel and dentine a maximum of $100\mu\text{m}$. At this distance the sharpness and contrast of the image may be poor, the best images being derived from structures just below the surface ($<20\mu\text{m}$). The technique generates significant

improvements in resolution, lying somewhere between that of conventional light microscopy and transmission electron microscopy/scanning electron microscopy (Watson and Boyde 1987a,b). Recent developments have allowed both clinical imaging and improvements in resolution at significant depths within a sample (Watson and Boyde 1991; Watson 1997).

In this chapter, some of the practicalities and recent developments in confocal microscopy will be reviewed as well as other related optical techniques as applied to dental biomaterials research. Readers should also be aware that all microscopic techniques involve artefact and so appropriate references should be consulted (Watson and Boyde 1991; Watson 1997; Pawley 2006).

2.2.1 Sample preparation and mounting

The long accepted way to examine hard tissues for conventional light microscopy is by sectioning them with a diamond saw and then making thin ground sections (<100µm thick) of the tissue. These are then placed on slides in standard mounting media and observed using transmitted light illumination. Most confocal microscopes are of the 'reflected light' or 'epi-illumination' type so that samples can be imaged from their surfaces without the need for thin section preparation. This has major advantages when imaging biomaterials/tooth interfaces as relatively large intact tooth samples can be placed on the microscope stage. All that is required is to section the sample once and observe directly the subsurface structures, taking advantage of the optical sectioning characteristics of confocal microscopy. To get a good quality image it is best to use a fine diamond saw, running very slowly under water, to give the best surface finish possible in the 'as cut' condition.

It will be easier to image internal structures if the sample has been lightly polished, as the smear layer produced on sectioning the sample will not be acting as a light-diffusing structure. However, one then has to balance this potential disruption to the sample structure against improvements in image quality.

For subsurface analysis of the sample structure some sort of coupling or immersion medium will be required. Where indicated for the lens being used, cover slips will be necessary, but these need to be as thin as possible, so as to give maximum depth penetration when focusing in to the sample. Water can, of course, be used on a tooth and has the advantage of allowing experiments to continue with the sample without any problems of contamination by oil. However, oil immersion objectives, with refractive indices of tooth tissue and immersion medium well matched, will produce the best images. Further methods for mounting samples are given in Watson and Pilecki (1999).

2.3 Conventional fluorescence and reflection imaging

The simplest technique for using confocal microscopy in dental materials research is to highlight the distribution of components within an adhesive system with fluorescent labels. As mentioned previously, the principle of fluorescence is the absorption by a dye molecule of a photon that triggers the emission of another photon with a longer wavelength and lower energy. Most conventional fluorescence microscopy is undertaken with dyes excited in the ultraviolet (UV)–visible spectrum giving longer wavelength fluorescence, the difference in wavelength being called the ‘Stokes shift’ after Sir George Stokes (1819–1903). When a molecule or atom absorbs light, it enters an excited electronic state. The Stokes shift occurs because the molecule loses a small amount of the absorbed energy before re-releasing the rest of the energy as luminescence or fluorescence, depending on the time between the absorption and the re-emission. This energy is often lost as thermal energy.

In fluorescence labelling experiments, it is important to be aware of any potential artefacts that may arise, taking care to use control experimental labelling techniques (Watson, 1997). While many researchers are only aware of the fluorescence imaging capabilities of confocal microscopes, the value of the back-scattered or reflected light signal should not be ignored, especially when produced using an incoherent light source with a tandem scanning microscope (TSM) (Watson and Boyde 1987a,b,c). Many of the resin-based adhesive systems will affect the refractive and reflective properties of dentine and enamel, so that it is possible to see differences due to the hybrid layer without recourse to fluorescent dyes. It is also possible to apply high-speed imaging techniques for the study of rapidly changing events such as cutting of hard tissues (Watson and Cook 1995; Watson *et al.* 2000b) and the fracture of adhesive interfaces (Sidhu and Watson 1999; Griffiths *et al.* 2000).

2.4 Imaging water transit in materials

The seal of restorative materials can be judged using high-resolution micro-leakage studies or, alternatively, micro-permeability studies (Griffiths *et al.* 1998). Modern simplified adhesives exhibit severe water sorption, which lowers the mechanical properties of hydrophilic resins and promotes hydrolysis of resin and collagen fibrils (Tay *et al.*, 2004 and also Chapter 5 of this volume). The term ‘micro-permeability’ was first used by Sidhu and Watson (1998) in the evaluation of the interfacial characteristics of resin-modified glass ionomers. Fluid movement from the pulp chamber towards the resin-bonded dentine interface through dentinal tubules can be detected by using a solution of rhodamine B placed in the pulp chamber. Such movement

provides an indication of the relative sealing ability of the bonded interface and the hydrophilicity of the dentine adhesive (Griffiths *et al.*, 1999). These studies revealed important information regarding bonded-layer interfacial porosity, especially in samples apparently free of interfacial gaps. The extent of permeability is dependent upon the penetration of the adhesive components into etched dentine and on the development of porosities or gaps in the bonded interface resulting from polymerization shrinkage of the primer, adhesive, or resin components. Using confocal laser scanning microscopy, fluorescent dyes have been shown to penetrate through dentine towards the interfacial region thus allowing evaluation of micro-permeability in the bonded interface. In this method, fluorophore presence would demonstrate possible routes for micro-permeability either around resin tags, through the porous base of the hybrid layer, and along the interface between the hybrid layer and the adhesive agent. Use of this technique also allows identification of resin tags that might have separated from or pulled away from dentinal tubule walls, resulting from stress developed during photo-polymerization of resin composite. Such separation will create a microscopic gap of sufficient size to make the interface permeable (Griffiths *et al.* 1999).

The importance of resin tags within dentinal tubules in achieving a successful seal is unknown, but the link between the intra-tubular dentine and the resin may be of prime importance when determining restoration micro-permeability (Prati *et al.* 1995; Sauro *et al.* 2007a,b; see also Chapter 5 of this volume for an in-depth discussion of this problem). Similarly, impregnation of the primer and adhesive into the conditioned inter-tubular dentine surface is relevant not only for maximizing bond strength, but also for providing interfacial sealing. Griffiths *et al.* (1999), using a control adhesive system that retained a modified smear layer, confirmed that fluorescent dye could penetrate the porosities within the smear layer as well as the bonded interface. These findings relate to the term ‘nanoleakage’ and suggest possible pathways for permeability through the hybrid zone itself. Nanoleakage occurs in the absence of gaps through nanometre-sized spaces of approximately 0.02 μm and starts at the bottom of the hybrid layer, where resin monomers interface with decalcified dentine, and spreads throughout this structure (see Chapter 3 of this volume).

Using confocal microscopy, Dörfer *et al.* (2000) observed fluid movement at the junction of the adhesive resin and hybrid layer during flexure of the restoration and the tooth. Such flexure may promote mechanical and chemical degradation of the cured resin and bonded interface, and may accelerate washout of water-soluble monomers.

Fluorescent dyes placed in the pulp chamber must be soluble in distilled water or in phosphate-buffered saline. Otherwise, the fluorophores will phase-separate and not be able to reach the interface. Use of solvents, such as alcohol, should be avoided as they can impair the integrity of the hybrid

layer, causing leaching of uncured adhesive system components (Kaga *et al.* 2004) or dissolution of poorly formed polymer networks (Pioch *et al.* 1997) which may then lead to formation of image artefacts. Thus, confounding factors may cause misinterpretation of nanoleakage. Most of the dyes used are very small and may permeate throughout dentine and erratically permeate the hybrid layer and adhesive layer.

From the preceding references, it can be seen that the micro-permeability of the hybrid layer has generally been studied without the use of dye mixed with adhesive systems. Incorporating dyes into dentine-bonding agents can increase the scope of the imaging technique because the morphology of the hybrid layer and the extension of resin tags can be analysed. The pulpally placed dye can reach the bonded interface producing contrast to the dye-labelled adhesive. The penetration paths of the different dyes can therefore be observed by recording the distribution of the different fluorescent-labelled agents. Thus, individual structures within the same specimen can be better recognized and analysed (Pioch *et al.* 2001). As always, care should be taken in the interpretation of results, with the correct use of controls and careful analysis of the interaction between the dye and the adhesive material (Watson 1997; D'Alpino *et al.* 2006a). However, this type of study would be better undertaken using FLIM (see below).

Using two different marker systems and confocal microscopy, it is possible to evaluate the effect of pulpal pressure on adhesive water sorption and on the sealing ability of current adhesive systems (Sauro *et al.* 2007b). The following describes a technique for achieving this, based upon the silver staining nanoleakage technique of Sano (see chapter 3) and the micro-permeability methods outlined above.

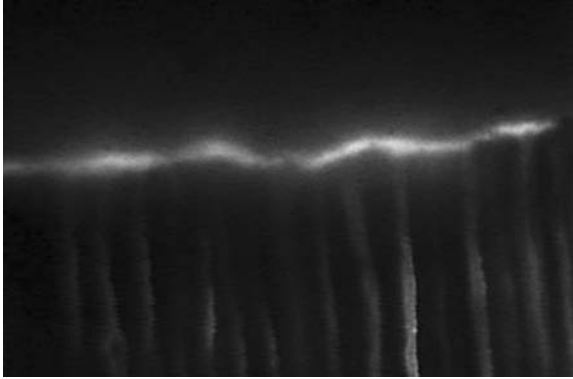
Deep dentine crown segments with remaining dentine thickness of 0.7–0.8 mm are made by removing the occlusal enamel using a slow-speed, water-cooled diamond saw. The roots are then removed by making a parallel cut 1 mm beneath the cemento-enamel junction. Pulpal tissue should be removed, taking care to avoid damage of the pre-dentine surface. A standard smear layer can be created using 180 grit silicon carbide papers. The sample is then attached to a PerspexTM support that is perforated by an 18 gauge stainless-steel tube and then connected to a hydraulic pressure device delivering 20 cm H₂O pressure. Different classes of adhesive materials can then be applied according to the manufacturer's instructions while connected to the permeability device and during simulated intra-pulpal pressure delivery. Following light-curing, a conventional and basic (i.e. slightly alkaline) ammoniacal silver nitrate solution is delivered at 20 cm H₂O for 24 h. Subsequently, a rhodamine solution is delivered for 3 h using the same pressure device as described by Griffiths *et al.* (1998). The samples are then sliced into 1 mm slabs, lightly polished using 1200 grit silicon carbide paper, ultrasonicated for 2 min and photodeveloped under UV as suggested by Tay

et al. (2002). Finally, the samples are washed using de-ionized water for 30s and further ultrasonicated for 2min. The examination is undertaken in reflection and fluorescence mode using a $\times 100$ oil immersion lens with a TSM/confocal laser scanning microscope (CLSM) and the appropriate excitation/emission filters.

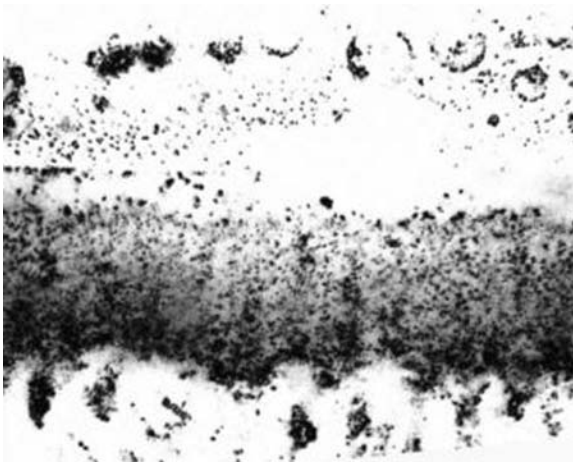
Images can show the diffusion of the rhodamine dye through the adhesive interface where it is permeable from the pulp and the dentinal tubules, while the silver staining technique shows the presence of nanoleakage within the hybrid layer and water trees within the adhesive components as a sign of water sorption. As an example, the 3M ESPE silorane bonding system can be used to show the relative sealing ability of different components of an adhesive system (3M ESPE Seefeld, Germany). This adhesive is a self-etch two-step system that is used to bond an intensely hydrophobic silorane composite to wet dentine. After adhesive application on deep sound dentine under 20 cm H₂O, simulated pulpal pressure deposits of silver grains were visible in the hybrid layer and within the thickness of the primer layer while the adhesive layer was absolutely free from silver penetration and water trees (Fig. 2.1). The confocal fluorescence evaluation showed rhodamine penetration only within and at the bottom of the hybrid layer (Fig. 2.2). However, when the 3M ESPE Scotchbond 1XT adhesive



2.1 Silver-stained reflection confocal image of silorane adhesive and dentine showing some silver grains (black dots) dispersed throughout the primer layer and hybrid zone, but with no uptake by the adhesive (top of image) [$\times 100/1.4$ numerical aperture (NA) oil immersion objective; fieldwidth, 60 μ m].



2.2 Fluorescence confocal image of silorane adhesive showing fluorescent dye restricted to the hybrid zone and minimally through the primer layer. No dye uptake by the adhesive film ($\times 100/1.4$ NA oil immersion objective; 546 nm excitation; 600 nm emission filter; fieldwidth, $60\mu\text{m}$).



2.3 Silver-stained reflection confocal image of Scotchbond 1XT adhesive showing extensive silver grains (black dots) dispersed throughout the primer layer, hybrid zone, and adhesive (top of image) ($\times 100/1.4$ NA oil immersion objective; fieldwidth, $60\mu\text{m}$).

(total-etch/all-in-one system) was applied under simulated pulpal pressure, it was possible to observe an increased presence of silver grains and the extension of water trees within the hybrid layer and along the full thickness of the adhesive. Silver diffusion also occurred between the composite and adhesive thereby indicating the high water permeability of this kind of system (Fig. 2.3). The confocal fluorescence evaluation similarly showed

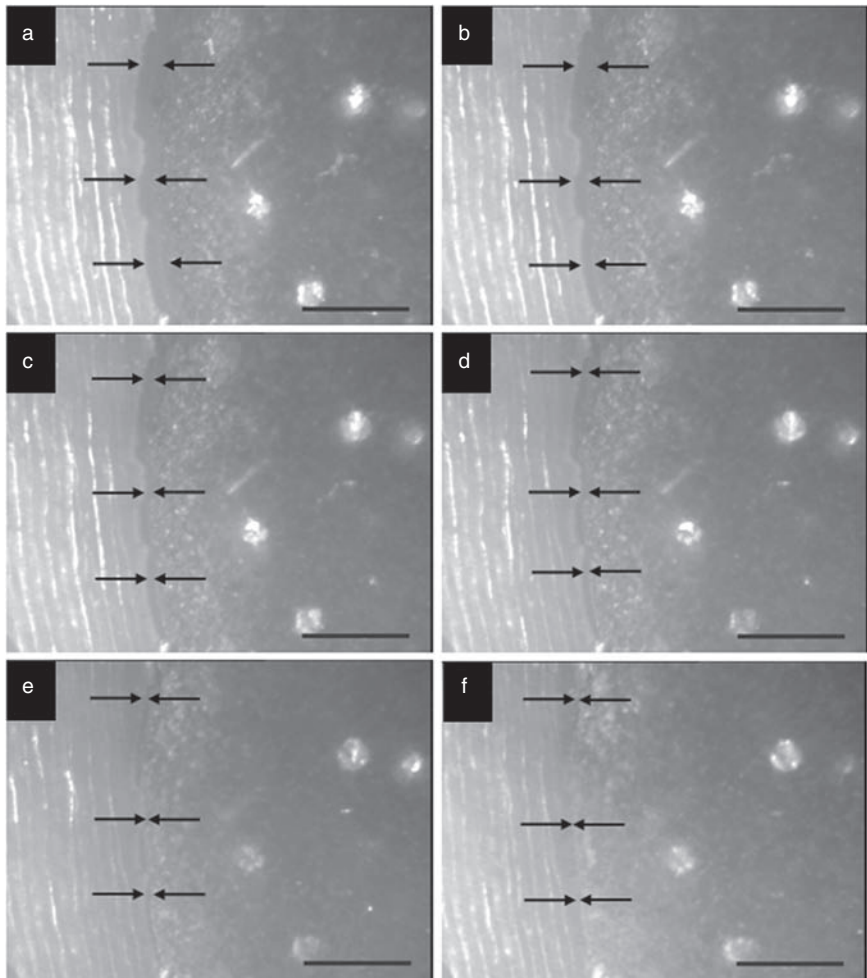


2.4 Fluorescence confocal image of Scotchbond 1XT adhesive showing fluorescent dye throughout the hybrid zone and particularly noticeable within the adhesive, highlighting the bubbles due to water transit (top of image). The blisters correlate well with the tubular openings ($\times 100/1.4$ NA oil immersion objective; 546 nm excitation; 600 nm emission filter; fieldwidth, $60\mu\text{m}$).



2.5 Combined reflection and fluorescence image of S3 Bond and dentine. Silver grains are showing as white reflective dots with grey background showing fluorescence from rhodamine also showing water permeation. The adhesive interface shows a gap at the hybrid zone ($\times 100/1.4$ NA oil immersion objective; 514 nm excitation; 600 nm emission filter).

rhodamine penetration within all the thickness of the adhesive and also between the adhesive and composite, with water blisters being more easily discerned in the adhesive layer superficial to the hybrid zone (Fig. 2.4). The presence of water bubbles throughout the adhesive correlated well with the dentinal tubule orifices (Fig. 2.4).



2.6 A series of confocal reflection images showing the uptake of water and consequent swelling of a fully reacted glass ionomer-composite 'Reactmer': the crack visible within the material-tooth interface closed over 600s ($\times 50/1.00$ NA water immersion objective. Scale bar, 50 μm).

Combination of the fluorescence and reflection image of the dye uptake and silver grain penetration from one field of view, in one image, shows the different absorption paths present in an adhesive material; as shown by the self-etch adhesive S3 Bond (Kuraray, Japan). In this image, a gap has formed between the adhesive and the substrate (Fig. 2.5): the fluorescence image is usually superior for showing the presence of bubbles or blisters within the material, while the silver staining technique shows nanoleakage pathways through the components of the adhesive interface.

2.5 Imaging moisture-sensitive materials

Confocal microscopy can be used to examine below the surface of samples without dehydration damage due to vacuum. However, studies of drying-out effects on materials can be made using dry objectives (Griffiths *et al.* 2000). The maturation of glass-ionomer cements (GICs) can be a relatively slow process and varies significantly between different types (Watson 1990). Measuring the rate of crack opening and closure in different environments will give an indication of their maturation rate. Experimental set-ups have studied this water loss and water uptake in immature cements. Subsurface imaging of cement that is drying out is difficult when using a dry objective, because of surface reflections; using an immersion medium on the sample can reduce these. If oil is placed below the cover glass, the sample will remain hydrated, but if glycerine is used, the material will lose water to the hygroscopic glycerine. The glycerine can be changed subsequently for water and the effects of water influx on the same sample can then be studied (Sidhu and Watson 1997; Watson *et al.* 1998; Sidhu *et al.* 2002). Such experimental procedures can also be applied to imaging the water uptake and the swelling of other hybrid materials such as poly-acid-modified composites and partially reacted or fully reacted glass ionomer–composite-type materials such as ‘Reactmer’ (Shofu Dental, Japan). It is evident that the fully reacted glass ionomer–composite materials are unstable in a changing aqueous environment (Fig. 2.6).

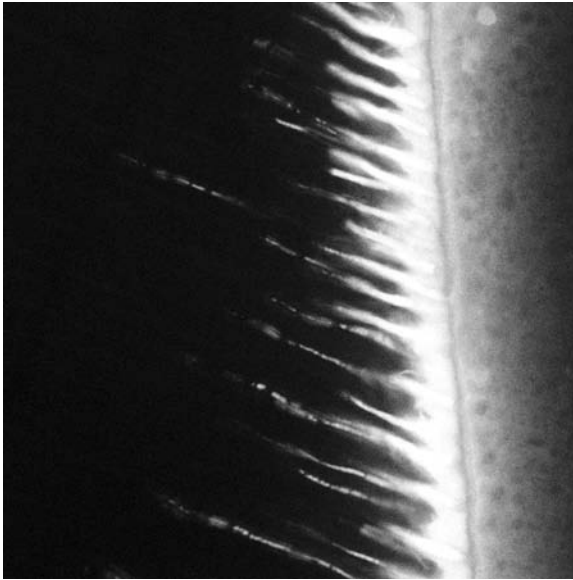
2.6 Multi-photon imaging: deeper penetration

The main difficulty in confocal imaging of dental materials is related to the significant light-scattering properties of the hard tissues and the tooth-coloured materials used to restore them. The ability of light to penetrate a hard tissue–biomaterial-type sample will self-evidently depend upon its translucency, with more difficulties in penetrating materials with great opacity. When focusing deeply into a sample, reflective or opaque features will interfere with light passing into, and returning from, the focused-on plane. A signal may be returned from quite significant depths (up to 200 μm), but will not always show adequate detail.

Fluorescence confocal imaging will work well when examining discrete, isolated, structures within an interface. Visualizing features such as dentine tubules impregnated with fluorescent-labelled resin will be relatively easy if regions immediately above or below the plane of focus are not heavily dosed with fluorescent dye (Sidhu and Watson 1997). Indiscriminate fluorescent dye excitation by the illuminating light source can produce a strong signal that may overwhelm weaker signals from deeper planes of focus.

Two-photon laser fluorescence microscopy is a comparatively new form of far-field fluorescence optical microscopy, having first been reported in dental materials research in 2000 (Watson *et al.* 2000a; D'Alpino *et al.* 2006b). Commercial instrumentation is very similar to laser scanning confocal microscopy. However, the continuous-wave laser light source is replaced by a mode-locked titanium:sapphire laser operating in the near-infrared range with femtosecond (10^{-17}) pulses. A conventional system uses a light source emitting a continuous intensity of a few milliwatts, whereas a two-photon system has peak intensities at kilowatt levels. It is this combination of very high power over a very short time period that allows the two-photon mode of fluorescence excitation to occur. The laser produces tens of kilowatts of peak power in a series of low-energy pulses, which are approximately 10 nJ per pulse. The laser is tuned to a wavelength about twice that of the intended absorption wavelength of the fluorescent sample, which normally requires a nonlinear two-photon (or more) process to be excited (Diaspro and Sheppard 2002). The energy of two photons may be absorbed simultaneously by the fluorescent molecule and the energy is irradiated as a single photon. Thus, the emission spectrum has a lower limit of approximately half the excitation wavelength. Since the cross-section for the two-photon process varies as the inverse fourth power of the distance from the focus, only at the focal point will there be enough energy to excite fluorescent dyes with this long-wavelength light. This will therefore cause them to emit light of a shorter wavelength, i.e. the reverse of normal (Watson 1994; Pioch *et al.* 1997). Thus, the need for pinholes is reduced because there is virtually no fluorescence outside of the focal plane. Two-photon (or multi-photon) imaging also offers the potential advantage of greater depth penetration, because increase in illumination wavelength (e.g. 450 nm/blue to 800 nm/infrared) will improve depth penetration.

In order for two-photon excitation to be more effective, new fluorescent dyes have been developed that produce an optimal fluorescence output for low illumination intensities (Denk *et al.* 1990). APSS dye (4-[*N*-(2-hydroxyethylamino)styryl]-*N*-methylpyridinium tetraphenylborate) has been developed for this purpose and attachment to resins such as hydroxy ethyl methacrylate (HEMA) (Bhawalkar *et al.* 1996). APSS dye can also be excited using conventional blue (488 nm) light, with yellow (520 nm) emission (Sidhu *et al.* 2002) (Fig. 2.7). Rhodamine, fluorescein, and other 'conventional' fluorophores may leach from the material they are labelling, being readily alcohol- or water-soluble. However, this potential artefact can be checked easily using a variety of control techniques, while the correspondence of confocal images with those derived from other imaging techniques is very high (Watson 1997; Sidhu and Watson 1997). Dye movement can be used as a useful indicator of dynamic events in a tooth-restoration interface.



2.7 Two-photon excitation fluorescence image (excitation, 890 nm; emission, 510 nm) of the HEMA in Scotchbond 1XT adhesive labelled with APSS dye. Due to the high efficiency of this dye, this high-resolution (1024×1024 pixels, $156 \times 156 \mu\text{m}$) image was recorded in 10 s and has a lateral resolution of 760 nm.

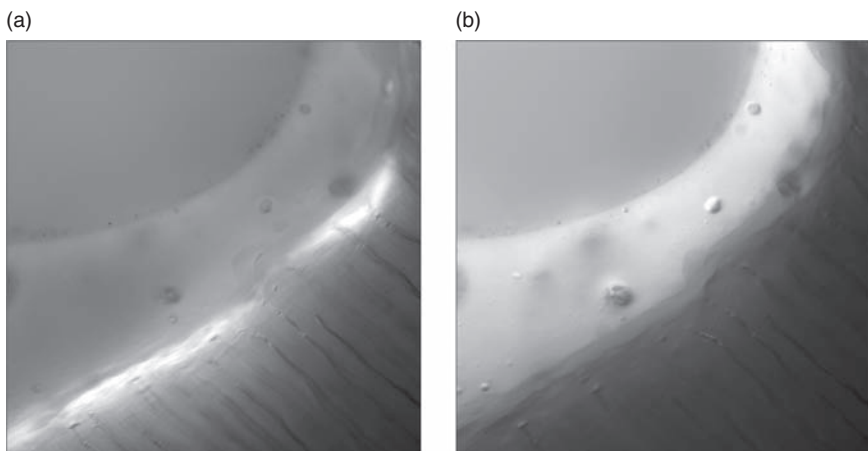
When imaging these adhesive interface samples, two-photon excitation gives twice the depth penetration ($<120 \mu\text{m}$), and better resolution of fine detail at this depth, than conventional confocal microscopy. Volume reconstructions are therefore more likely to reflect accurately the structure being imaged, without degradation due to problems of depth penetration of the illuminating light. Resolution of fine structures (e.g. lateral dentine tubules of $0.5 \mu\text{m}$ diameter) can readily be achieved with the new imaging technique at deep focal planes, where normally these can only be resolved very close to the section surface with conventional confocal imaging. Even so, superficial features, which are strong reflectors, can block light transmission to the focused-on plane or interfere with the fluorescence signal from the labelled material.

2.7 Fluorescence lifetime imaging

In standard fluorescence imaging, a sensitive detector, such as a cooled charge-coupled device (CCD), images emission from a fluorophore. Steady-state imaging suffers from the fact that fluorescence signal intensity is extremely dependent on the intensity of the excitation light and the concentration of fluorophore. Fluorescence lifetime is, however, independent

of fluorophore concentration, but dependent on local environment. FLIM thus allows researchers to obtain precise quantitative data about both fluorophore distribution and local environment. Two principal approaches to FLIM implementation exist: one in the time domain, the other in the frequency domain. For time-domain measurements, a laser or light-emitting diode (LED) excites the sample with femtosecond to nanosecond pulses. A gated detector, typically an intensified CCD (ICCD) camera system, captures the exponential decay of the fluorescence. In a simple situation, the investigator can compute the lifetime of a fluorophore with single-exponential decay by acquiring only two images at two different points in time after the excitation. Further references should be examined for an explanation of frequency domain imaging (Festy *et al.* 2007).

The application of FLIM to the imaging of adhesive interfaces in dental materials allows improved discrimination of different dyes and adhesive components, as can be seen in Fig. 2.8. In these images of SE Bond adhesive (Kuraray, Japan) the primer was labelled with Lucifer yellow and the bonding resin with rhodamine. Water blisters can be seen between the hybrid layer and the adhesive. However, with the correct selection of dyes with sufficient separation in excitation and emission wavelengths, coupled with correct filter arrangements, a component distribution can be crudely assessed using conventional fluorescence microscopy: Fig. 2.8 shows a low-magnification view of the adhesive interface imaged with wide field fluorescence microscopy (blue excitation–green emission for the Lucifer yellow; green excitation–red emission for the rhodamine). However, there

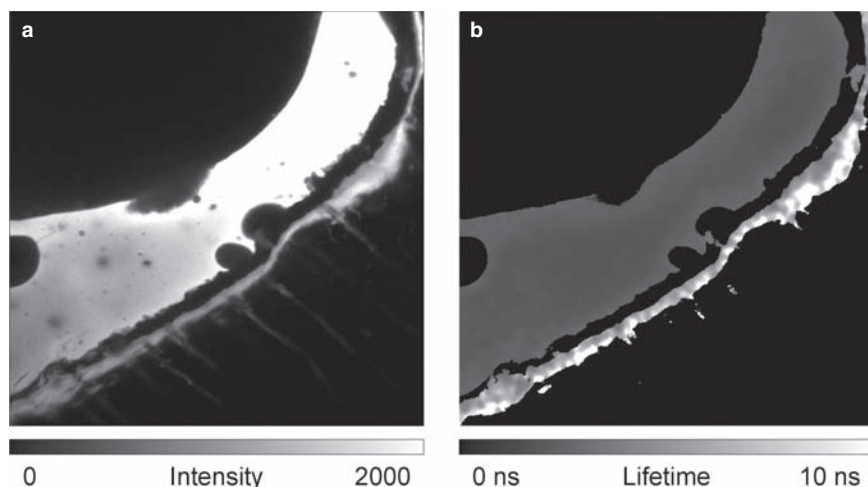


2.8 Low-magnification view of the SE Bond dentine–adhesive interface imaged with wide field fluorescence microscopy: *a* Blue excitation–green emission for the Lucifer yellow; *b* green excitation–red emission for the rhodamine.

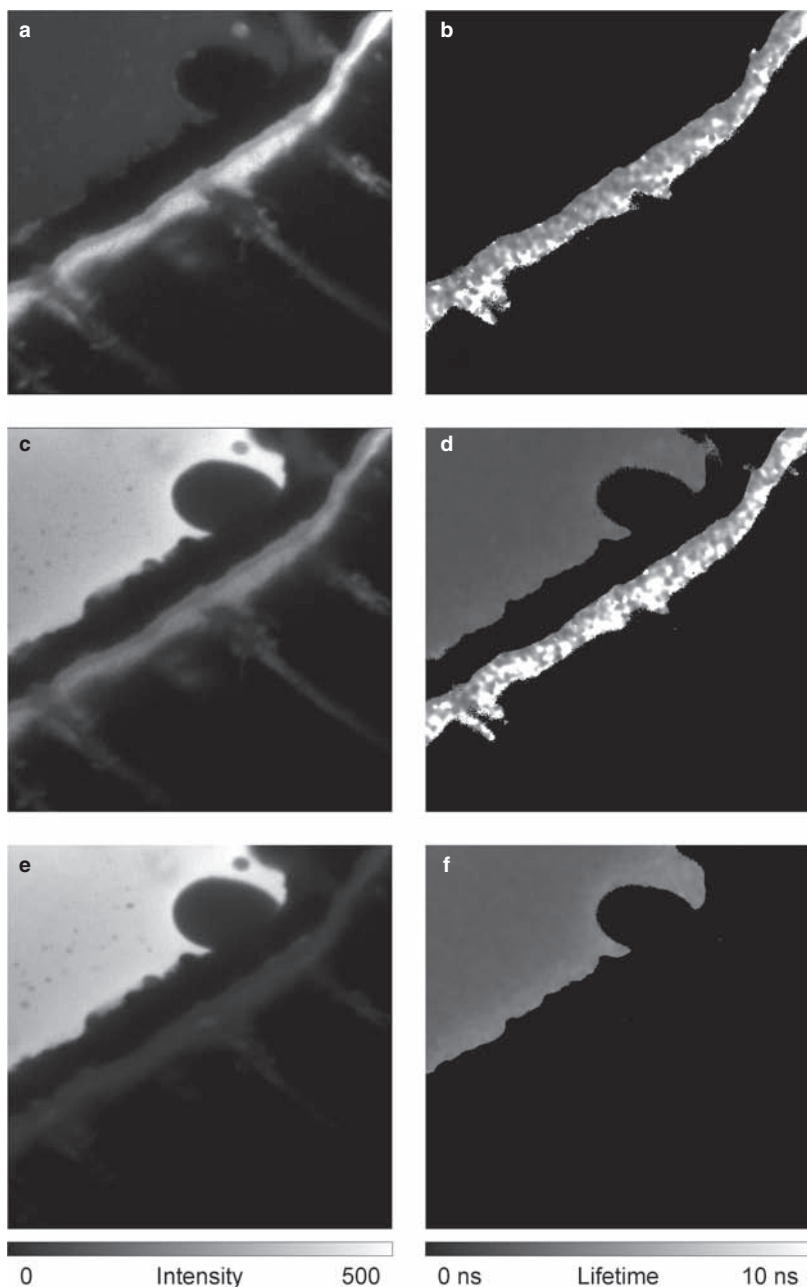
is a lack of resolution in this non-confocal view and some fluorescence cross-talk.

Figures 2.9a and 2.10a, c, and e show the distribution of the adhesive components with fluorescence separation being achieved by careful use of emission filters with the two-photon excitation of the fluorescent dyes. However, the FLIM images allow a more rigorous separation of the adhesive components as these are derived from the difference in fluorescence decay characteristics of their respective labels. A small amount of mixing between the adhesive with the primer is visible in the superficial region of the hybrid zone, as seen in Figs. 2.10b and d.

Most importantly, FLIM can allow weak fluorescence derived from the dental substrate itself to be discriminated from fluorescent dyes that may have similar spectral characteristics or an overwhelmingly greater fluorescence efficiency or intensity. It is not the fluorescence intensity that is recorded for the substrate but its decay rate. Applications such as determining adhesive penetration and hence bonding mechanisms to carious dentine by using fluorescently labelled adhesives and carious dentine autofluorescence are now possible (McConnell *et al.* 2007), where previously it would have been difficult to detect the weak autofluorescence signal in the presence of a dye-labelled adhesive.



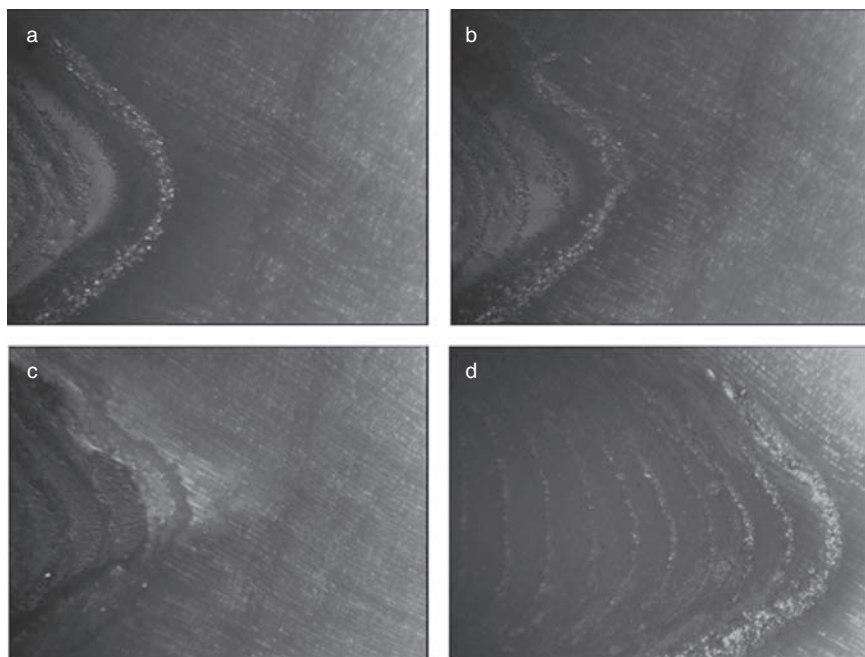
2.9a Fluorescence intensity alone does not permit correct dye identification as the dyes have similar emission intensity levels when illuminated with two-photon absorption at 890 nm and fluorescence emission at 560 nm. **b** The FLIM image shows a strong contrast due to the large difference in fluorescence decay between Lucifer yellow and rhodamine ($\times 40/1.4$ NA oil immersion objective; fieldwidth, 156 μm).



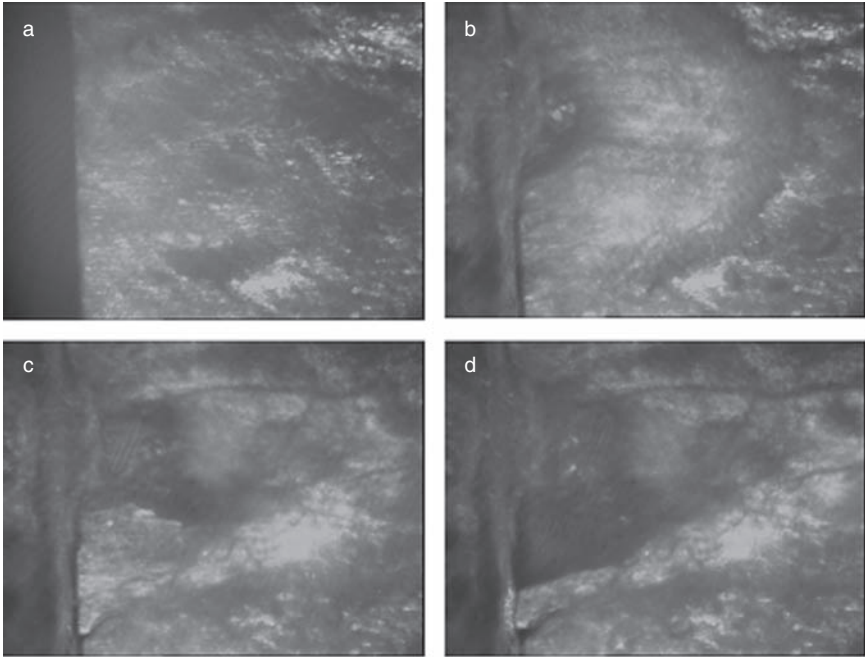
2.10 Same sample as in Figs 2.8 and 2.9: *a* 510 nm fluorescence emission so that only the Lucifer yellow-labelled primer remains visible; *b* the average fluorescence lifetime of Lucifer yellow is 5.3 ns; *c* Fluorescence emission wavelength of 560 nm does not discriminate between the two dyes; *d* FLIM shows better discrimination of the adhesive components; *e* The 610 nm fluorescence emission selectively shows the rhodamine-labelled primer; *f* indicates that the rhodamine average fluorescence lifetime is 2.8 ns, showing excellent discrimination of the adhesive (two-photon absorption at 890 nm. $\times 40/1.4$ NA oil immersion objective; zoomed $\times 3$; fieldwidth, 52 μ m).

2.8 High-speed imaging of dynamic events within materials

Imaging of fracture events within materials can be undertaken using video rate confocal microscopy. Previous studies have examined the interfacial failure of resin-modified glass ionomer cements and resin-based materials with dentine (Sidhu and Watson 1999; Griffiths *et al.* 2000). The TSM has been employed extensively for the imaging of bur-tooth cutting interactions (Watson and Cook 1995; Watson *et al.* 2000b), imaging of air abrasion cutting (Cook *et al.* 2001) and, more recently, pilot studies have begun to examine the effects of lasers, such as erbium YAG (yttrium aluminium garnet) on tooth tissue, using video confocal imaging techniques. This is technically somewhat difficult as there is a significant risk of damage to the end lens of the microscope objective using such cutting techniques. Current configurations of the microscope have used '*in vivo*' long focal range objectives in order to separate the cutting laser beam from the lens system of the microscope. These lenses have a working range of up to 8mm and have



2.11 Dentine lased with erbium YAG laser at 250mJ, 7pps, 10 pulses in total (25 frames per second): *a* Surface after two pulses; *b* during the next pulse; *c* after four pulses; *d* final image of dentine showing the effect of sequential pulses ($\times 24/0.60$ NA glycerine immersion objective; fieldwidth, 460 μ m).



2.12 Enamel ablation with 350 mJ, 10 pps, 5 pulses (25 fps). Progressive structural damage is shown ($\times 24/0.60$ NA glycerine immersion objective; fieldwidth, $460\mu\text{m}$).

internally focusable elements to select the plane of tissue on which to focus (Watson *et al.* 1992; Watson 1994). The laser energy pulses can be seen ablating the tooth tissue and the pulses may also show debris fields along the cutting path. Optical changes within the substrate may also be observed just below the cut surface, as a function of removal of tubular dentine structure as well as melt-derived material indicating each laser pulse (Fig. 2.11). Severe cracking of enamel was also visible following erbium YAG ablation (Fig. 2.12). Recording rates can currently be <60 frames per second (twice video rate), but there is clearly a need for increased speed of imaging and recording: a feature becoming more available with better EM-CCD camera sensitivity and ever increasing computing power.

2.9 Conclusion

Microscopical techniques have an obvious place in the evaluation of biomaterials. Thirty years ago, light microscopy was virtually written off as having insufficient resolution. The advent of confocal microscopy 20 years ago has reversed this trend and indeed optical imaging techniques have

undergone a renaissance, especially within the biological sciences, for high resolution imaging. The materials–biological science interface offers a unique experimental envelope for pushing the development of new optical microscopic techniques. The local environmental advantages for the specimen enable experiments to be undertaken with reduced preparation artefact, while modern developments can take resolution beyond what was once thought to be the limits for the wavelengths employed.

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Electron microscopy for imaging interfaces in dental restorations

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3.1 The transmission electron microscope (TEM)

3.1.1 Introduction

Electron microscopy (EM) has played an important role in the field of dental biomaterials for many years. The transmission electron microscope (TEM) is the instrument that is most capable of elucidating the ultra-structural morphology of the resin/tooth interface produced by dental adhesives, with high resolution and reliability. EM can be used to explore to the level of collagen fibril cross-banding in dentine (nanometer resolution), which is beyond the resolution limits of most conventional light microscopical techniques.

A normal TEM basically consists of four systems.

- 1 The illuminating system to produce the electron beam and direct it onto the sample; the system consists of the electron gun and the condenser lens.
- 2 The imaging system, which consists of a series of electromagnetic lenses that produce the final magnified images of the sample.
- 3 The image recording system, which consists of the observation screen and photographic film and converts the electron image observed on a fluorescent screen into a permanent record.
- 4 The high-vacuum system to remove all gases from the column that would reduce resolution (Gabriel, 1982). Recently, digital image recording systems utilizing a high-resolution charge-coupled device (CCD) camera have been used instead of photographic films.

Transmission electron microscopy involves the irradiation of the whole specimen, which is thin enough to transmit at least 50% of the incident electrons (Bancroft and Stevens, 1996). The emergent beam of transmitted electrons is focused by a system of lenses to form a magnified, two-dimensional image of the specimen. The major advantage of transmission electron microscopy is its high resolving power. The maximum obtainable

resolution is generally 1–2 nm for most biological materials but is limited by the nature of the specimen and the techniques involved in specimen preparation (Van Meerbeek *et al.*, 2000).

TEM examination of the interaction of adhesives with tooth substrates, especially dentine, was begun in the mid 1980s (Nakabayashi and Watanabe, 1983; Nakabayashi, 1985; Kiyomura, 1987; Watanabe and Nakabayashi, 1987). Since then, transmission electron microscopy has brought more details of the adhesive/dentine interface, such as: the complex process of hybridization (Eick *et al.*, 1991; Nakabayashi *et al.*, 1992, Van Meerbeek *et al.*, 1993, 1996, 1997, 1998a, 1998b, 2000, 2003, 2005, 2006; Koshiro *et al.*, 2006); the so-called wet-bonding technique (Kanca, 1992a, 1992b; Gwinnett, 1992; Tay *et al.*, 1994, 1995, 1996a, 1996b, 1996c, 1997; Perdigao *et al.*, 1999); nano-leakage phenomenon (Sano *et al.*, 1995a, 1995b; Tay *et al.*, 2002a, 2002b; Van Meerbeek *et al.*, 2005); water-treeing phenomenon (Tay *et al.*, 2002c; Tay and Pashley, 2003); *in vivo* and *in vitro* degradation of the dentine/adhesive interfaces (De Munck *et al.*, 2002; Koshiro *et al.*, 2005; Inoue *et al.*, 2005); and so on (see Chapter 4 of this volume). Recently, transmission electron microscopy has also been used to observe adhesive/enamel interfaces (Van Meerbeek *et al.*, 2000, 2003, 2006).

3.1.2 Specimen preparation

A representative method of preparing specimens of the adhesive/dentine interface for TEM observation is given below with some explanatory notes.

Dentine surface to be bonded

A tooth is sectioned horizontally using a low-speed diamond saw (e.g. Isomet, Buehler, Lake Bluff, IL, USA) under water coolant, to expose a flat mid-coronal dentine surface. The surface is then ground with 600-grit silicon carbide paper under running water to make a standardized smear layer.

Bonding treatment

The specimen is then subjected to the bonding treatment using the adhesive according to the manufacturer's instructions. After the bonding treatment, a flowable resin (e.g. Clearfil Protect Liner F, Kuraray Medical, Tokyo, Japan) is applied as thinly as possible and light-cured. The flowable resin protects the bonded surface and replaces the clinical use of a heavily filled resin composite, the filler particles of which will make thin-sectioning with a diamond knife quite challenging. The bonded specimen is then stored in water.

Demineralization (if needed)

The bonded specimen is cut to a mid-coronal dentine disk with a thickness of approximately 2 mm. The disk is then cut in half perpendicular to the adhesive/dentine interface. One half is further cut into three to four rectangular sections perpendicular to the interface. These sections are subjected to demineralization (demineralized specimens) in a solution of 10% (v/v) formaldehyde-formic acid (e.g. Surgipath Decalcifier I, Surgipath Medical Industries, Grayslake, IL, USA) for at least 36 h: this enables simultaneous demineralization and fixation if needed (Van Meerbeek *et al.*, 1996, 1998a; Koshiro *et al.*, 2005). The sections from the other half are kept in distilled water (non-demineralized specimens).

Thin-sectioning is more difficult in non-demineralized specimens because cutting should be made through the interface of a relatively soft resin material bonded to a hard, mineralized tooth substrate. Nevertheless, this technique undoubtedly provides the most reliable and convincing image of the resin/dentine interface.

Demineralization is performed to observe hard, mineralized tissues such as dentine. The minerals are removed and the tissues are softened, thereby making subsequent ultra-microtomy easier. The choice of decalcifier depends on the urgency of the experiment, the degree of mineralization, and the subsequent staining. Strong acidic decalcifiers such as nitric acid and hydrochloric acid are not appropriate to demineralize dentine for TEM observation. The most tissue-gentle and slow decalcifier is EDTA-2Na (ethylenediamine tetraacetic acid disodium salt) (Van Meerbeek *et al.*, 1993; Tay *et al.* 1996a, 1996b).

TEM observation combining non-demineralized with demineralized sections cut from the same tooth has a useful advantage in testing the resistance of the produced hybrid layer to demineralization. As a result of the demineralization, the collagen fibril network underneath the hybrid layer is deprived of its mineral phase. Differential take-up of heavy metal ions during staining, by the demineralized collagen fibril network, will indicate whether the hybrid layer has been enveloped by the resin during bonding hybridization and thus protected against demineralization; in other words, whether the adhesive resin has completely penetrated and polymerized, indicating the quality of the hybrid layer.

Fixation

After demineralization, the bonded specimens are subjected to chemical fixation overnight in 2.5% glutaraldehyde in 0.1 M sodium cacodylate buffer at pH 7.4 and 4°C. Chemical fixation is performed to stabilize and preserve the ultra-structure of the specimen. This needs to be accomplished as rapidly as possible, so that any changes are kept to a minimum. Fixation protects

the specimens against subsequent treatments – including rinsing, dehydration, staining, vacuum and exposure to the electron beam. Fixed specimens show less shrinkage in the last steps of dehydration as well as during infiltration and embedding (Hayat, 1986).

Glutaraldehyde (glutaric acid dialdehyde, $C_5H_8O_2$) is the best protein fixative for EM, although it cannot fix soluble proteins and lipids. It introduces both inter- and intra-molecular cross-links into protein macromolecules; these cross-links are irreversible. Sodium cacodylate buffer is one of the most commonly used buffers. This buffer contains arsenic which is a health hazard. Hands should be protected by disposable gloves, and eyes should be covered with gas-tight goggles. A fume hood should be used for weighing the reagent and preparing the buffer solution.

Dehydration

The fixed specimens are rinsed in 0.1 M sodium cacodylate buffer for 1 min with three changes, and then dehydrated in ascending grades of ethanol (50%, 75%, 95% and 100%) for 10 min each, with two changes. Rinsing before dehydration is needed to minimize the possible reaction between the fixative and the dehydrating agent. If possible, rinsing should be accomplished in the same buffer as that used with the fixative, to minimize differences in effective osmolarity. Dehydration is necessary as commonly used embedding resins are immiscible with water. Thus, all the free water from the specimens must be replaced with a suitable organic solvent before embedding. The water is removed by passing the specimens through a series of solutions of ascending concentrations of either ethanol or acetone.

Embedding

Dehydrated specimens are then immersed in 1:1 absolute ethanol–epoxy embedding resin (e.g. Epon 812, Polysciences, Warrington, PA, USA) for 4 h, followed by resin infiltration in 100% epoxy embedding resin for another 8 h, both with rotation at 4 rpm in a rotator (e.g. Taab Rotator type N, Taab Laboratories, PA, USA), and, finally, embedding of the resin-infiltrated samples in molds with 100% epoxy resin. The epoxy blocks are polymerized in an oven at 60 °C for 48 h.

Embedding has the function of infiltrating the specimens with a material that supports them without distortion but is still sufficiently elastic to be cut into thin-enough sections. This process starts by infiltration with a mixture of the dehydration reagent and the embedding medium, followed by infiltration with pure embedding medium, and also placing the tissue in a embedding mold, and finishes by polymerization of the embedding medium, usually by heat.

Epoxy resins are very toxic and cause dermatitis if directly touched, hands should therefore be protected with disposable gloves. Although epoxy resin is commonly used to stabilize fixed and dehydrated tissues in order to preserve the tissue integrity, to prevent artifact formation due to shrinkage and collapse, and finally to enable ultra-microtomy, non-embedded sections have the additional advantage that a specific location along the interface can be examined before and directly after demineralization of the section in order to judge the quality of the hybrid layer (Nakabayashi *et al.*, 1992; Van Meerbeek, 1997).

Cutting ultra-thin sections

Preparation of such thin specimens of good quality from a hard mineralized tissue like dentine is extremely difficult, and considerable experience is required to master the skill of sectioning. The most important factor is patience. Following polymerization of the epoxy resin, the tissue blocks are removed from the embedding mold. The blocks require trimming before thin-sectioning. The main purpose of trimming is to remove the excess resin surrounding the specimen at the tip of the block by shaving with a razor blade. After this rough trimming, specimens are then coarse and fine trimmed on an ultra-microtome (e.g. Ultracut UCT, Leica, Vienna, Austria) by using a glass knife or a discarded diamond knife until cutting thick sections of about 1 μm thickness. It is now ready for ultra-thin sections to be cut using a diamond knife (e.g. Diatome, Bienne, Switzerland) which is exceedingly sharp. After obtaining a straight ribbon floating on the surface of the liquid in the trough, i.e. a series of consecutively cut sections that have a gray interference color (approximate thickness, 60 nm) or silver (approximate thickness, 90 nm), the sections are collected on a grid.

The main disadvantage of using diamond knives are the cost of purchase and re-sharpening. When cutting hard tissue such as dentine (enamel is obviously harder), the knife edge is quickly damaged and rapidly needs re-sharpening.

Staining (if required)

The sections are, if required, positively stained with saturated 5% uranyl acetate for 20 min and with saturated lead citrate for 3 min before to being observed with a TEM. Positive (electron) staining increases the electron scattering power of biological specimens, because the specimens consist of low atomic number elements (carbon, hydrogen, oxygen and nitrogen) that have a relatively low electron scattering power and also because the epoxy resin possesses the same atoms as those constituting the tissues. As there is

little difference between the scattering power of the specimen and the resin, the TEM image lacks contrast. Introduction of heavy metal ions (osmium, uranium and lead) into either the tissue and/or the section increases the scattering power, thereby improving contrast. Specimen contrast can also be increased by using low accelerating voltages, a smaller objective aperture and thicker sections (Hayat, 1986).

The most common positive staining procedure for observing adhesive/dentine interfaces involves double staining of ultra-thin sections by the successive use of uranyl acetate and lead citrate. Because uranyl acetate reacts with phosphate ions, recent adhesives containing phosphate as a functional monomer, like di-HEMA (2-hydroxyethyl methacrylate) phosphate in Prompt L-POP (3M ESPE, St Paul, MN, USA) pick up heavy metals abundantly from staining, allowing their infiltration in the exposed collagen fibril network to be easily tracked (Van Meerbeek *et al.*, 2000).

The major issues in staining procedures are low specificity, contaminated staining solutions and incomplete rinsing. Specificity can be improved by carefully controlling the stain concentration, the pH and the duration of staining. Freshly prepared solutions should be used. All the staining solutions should be thoroughly removed by rinsing with distilled water; otherwise they will dry on the surface of the section and form precipitations (Hayat, 1986).

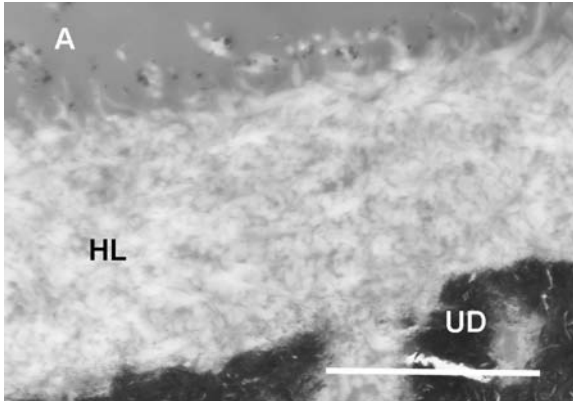
3.1.3 Typical transmission electron microscope images of adhesive/dentine interfaces

Some typical TEM images of various types of adhesive/dentine interface are shown in Figs 3.1 to 3.6. TEM images are always two-dimensional, and show the ultra-structure inside the specimen, whereas scanning electron microscope (SEM) images show three-dimensional surface ultra-morphologies. Moreover, TEM images originate from just a small area, therefore care should be taken to ensure that it is a representative area for the whole specimen. The most reliable information will be gathered when diverse microscopy techniques are combined.

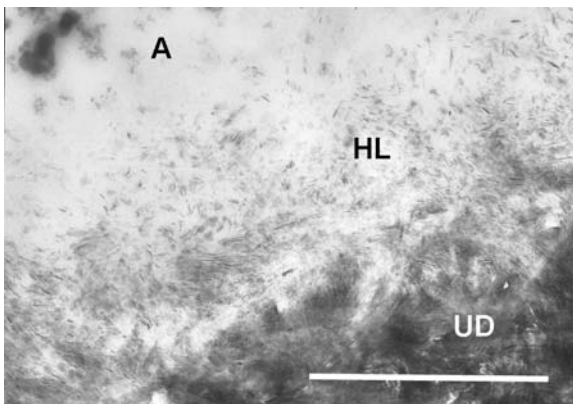
3.2 The scanning electron microscope (SEM)

3.2.1 Introduction

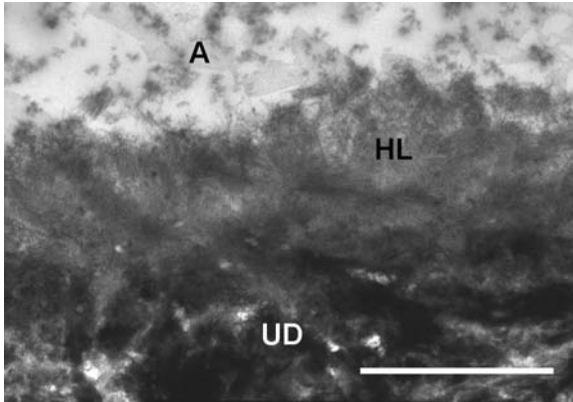
The scanning electron microscope (SEM) is a type of electron microscope producing high-resolution images of sample surfaces. The images created by an SEM have a three-dimensional black and white appearance with a sharp focus over a great depth of field. Generally, conventional light



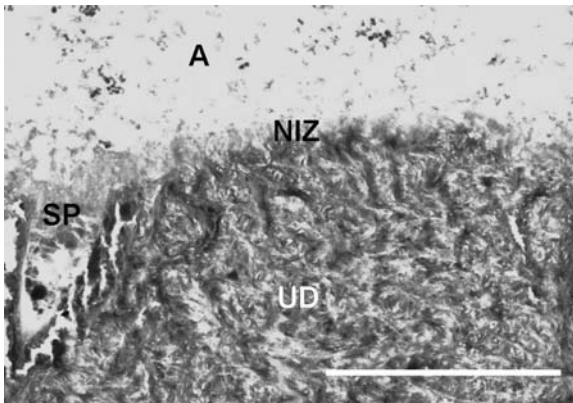
3.1 TEM photomicrograph of a non-demineralized, unstained section illustrating the interface between dentine and the 'strong' one-step, self-etch adhesive Absolute (Dentsply-Sankin, Tochigi, Japan). A 2–3 μm hybrid layer, not containing any residual hydroxyapatite crystals, is formed similar to that produced by an etch and rinse adhesive system using phosphoric acid as the etching agent. Note that a 'shag-carpet' appearance is clearly observed at the top of the hybrid layer. The collagen fibrils are directed towards the adhesive resin, resulting from actively rubbing the dentine surface with an acidic self-etching/priming/bonding agent. (A, adhesive resin; HL, hybrid layer; UD, unaffected dentine. Scale bar, 2 μm .)



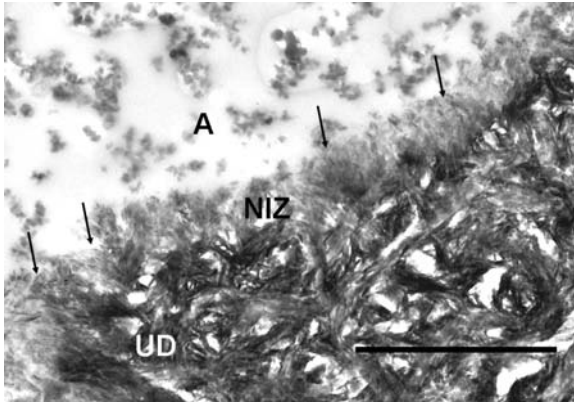
3.2 TEM photomicrograph of a non-demineralized, unstained section illustrating the interface between dentine and the 'mild' two-step, self-etch adhesive Clearfil MegaBond (commercially available as SE Bond outside Japan) (Kuraray Medical, Tokyo, Japan). Dentine was only partially demineralized without complete exposure of collagen fibrils (not visible on this image because they are covered by hydroxyapatite and the section has not been positively stained). Hydroxyapatite crystals are clearly observed within the hybrid layer. (A, adhesive resin; HL, hybrid layer; UD, unaffected dentine. Scale bar, 1 μm .)



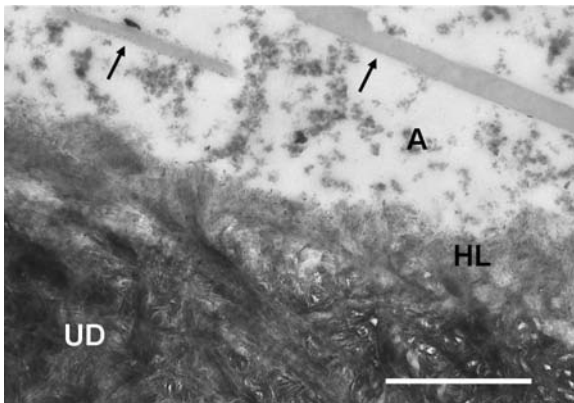
3.3 TEM photomicrograph of a non-demineralized, stained section of the interface between dentine and Clearfil MegaBond (SE Bond). Note that collagen fibrils are densely stained within the hybrid layer. (A, adhesive resin; HL, hybrid layer; UD, unaffected dentine. Scale bar, 1 μm .)



3.4 TEM photomicrograph of a non-demineralized, unstained section illustrating the interface between dentine and the one-step, self-etch adhesive G-Bond (GC, Tokyo, Japan). The superficial dentine is only slightly decalcified, and there seems to be no exposure of collagen fibrils. A smear plug is not removed, and resinous materials cannot be observed within the dentinal tubule. The thickness of the nano-interaction zone (NIZ) is approximately <300 nm. In the adhesive resin layer, micro-filler particles are seen. (A, adhesive resin; SP, smear plug; UD, unaffected dentine. Scale bar, 5 μm .)



3.5 TEM photomicrograph of a non-demineralized, unstained section illustrating the interface between dentine and the one-step, self-etch adhesive Clearfil Tri-S Bond (S3 Bond) (Kuraray Medical). Many hydroxyapatite crystals (arrows) are observed at the interface (within the NIZ) and there appears to be no exposure of collagen fibers. The thickness of the NIZ is approximately $<300\text{ nm}$. In the adhesive resin layer, micro-filler particles are seen. (A, adhesive resin; NIZ, nano-interaction zone; UD, unaffected dentine. Scale bar, $1\text{ }\mu\text{m}$.)



3.6 TEM photomicrograph of a non-demineralized, unstained section illustrating the interface formed at dentine by the two-step, self-etch adhesive Clearfil MegaBond FA (Kuraray Medical; this product is commercially available as Protect Bond outside Japan) containing the anti-bacterial monomer, 12-methacryloyloxydodecylpyridinium bromide (MDPB). The hybrid layer is very similar to that of Clearfil MegaBond (Fig. 3.2) because this adhesive is basically made from MegaBond. The existence of the NaF crystals (arrows) in the bonding resin layer is very specific to this product. The hybrid layer is about $0.5\text{ }\mu\text{m}$ wide and many hydroxyapatite crystals are observed within the hybrid layer. (A, adhesive resin; HL, hybrid layer; UD, unaffected dentine. Scale bar, $1\text{ }\mu\text{m}$.)

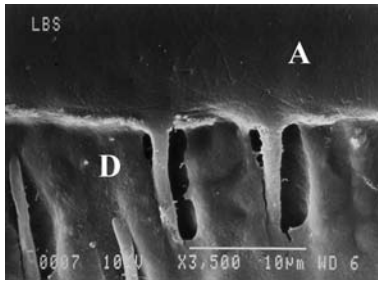
microscopes cannot create such high-resolution images. In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB_6) cathode and are accelerated towards an anode; alternatively electrons can be emitted via field emission (FE). Tungsten is ideal for electron emission because it has the lowest vapor pressure and highest melting point of all metals, thereby allowing it to be heated. The electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is focused by one or two condenser lenses into a beam with a very fine (1–5 nm sized) focal spot. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam in a raster fashion over a rectangular area of the sample surface. On striking the specimen surface, the scattered primary electron beam effectively spreads and fills a teardrop-shaped volume, known as the interaction volume, extending from less than 100 nm to around 5 μm into the surface. Interactions in this region lead to the subsequent emission of electrons which are then detected to produce an image.

X-rays, which are also produced by the interaction of electrons with the sample, may also be detected in an SEM equipped for energy-dispersive X-ray spectroscopy or wavelength-dispersive X-ray spectroscopy (Peters, 1985, 1987; Joy and Pawley, 1992).

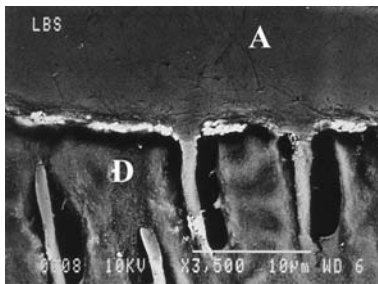
3.2.2 Detection of secondary electrons

The most common imaging mode monitors low-energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometers of the surface. The electrons are detected by a scintillator–photomultiplier device and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a digital image. This process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons ‘escape’ from within the sample. As the angle of incidence increases, the ‘escape’ distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus, steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Using this technique, resolutions of less than 1 nm are possible (Peters, 1985; Joy, 1992).

Figure 3.7 shows the secondary electron image of the resin/dentine interface using a silver nitrate staining technique. The surface of the specimen was highly polished with diamond pastes (6, 3 and 1 μm) and subsequently exposed to an acid/base treatment. After room drying and gold coating, SEM observation was performed. The acid- and alkaline-resistant layer



3.7 Secondary electron image of resin/dentine interface. (A, cured adhesive resin; D, dentine.)



3.8 Backscattered electron image of the resin/dentine interface. (A, cured adhesive resin; D, dentine.)

(hybrid layer) was observed between the cured adhesive resin (A) and underlying dentine (D). Silver penetration is just discernible at the base of the hybrid layer. However, because of the relatively low contrast using a secondary electron image, it was somewhat difficult to locate the exact sites that were stained with silver nitrate (Sano *et al.*, 1995a, 1995b).

3.2.3 Detection of backscattered electrons

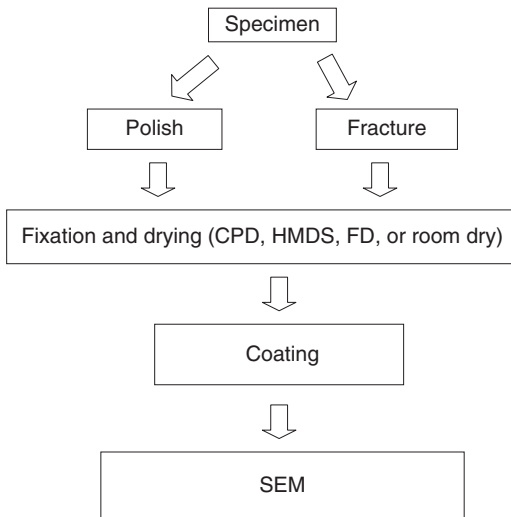
In addition to the secondary electrons, backscattered electrons can also be detected. Backscattered electrons may be used to detect contrast between areas with different chemical compositions. These can be observed especially when the average atomic number of the various regions is different; in effect atomic number contrast (Peters, 1985, 1987).

Figure 3.8 shows the backscattered electron image of the same resin/dentine interface stained with silver nitrate. White structures between the cured adhesive resin (A) and dentine (D) represent the metallic silver accumulation within the hybrid layer. Silver deposits are more clearly observed compared with Fig. 3.7, because the backscattered electron image

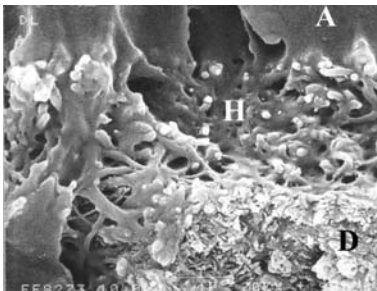
enhances the elements of high atomic number such as metallic silver (Sano *et al.*, 1995a, 1995b).

3.2.4 General procedures for scanning electron microscope observation

Figure 3.9 summarizes our procedures for specimen preparation for SEM observation. Generally, bonded specimens are polished (Fig. 3.7) or fractured (Fig. 3.10) through the bonded interface. Polishing is performed



3.9 Summary of specimen preparation for SEM observation CPD, critical point drying; FD, freeze drying; HMDS, hexamethyldisilazane.

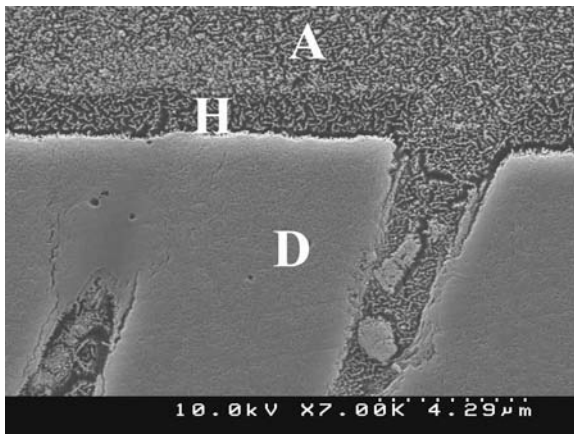


3.10 SEM image of the fractured resin/dentine interface. Cured adhesive resin (A), hybrid layer (H) and mineralized dentine (D) are clearly observed.

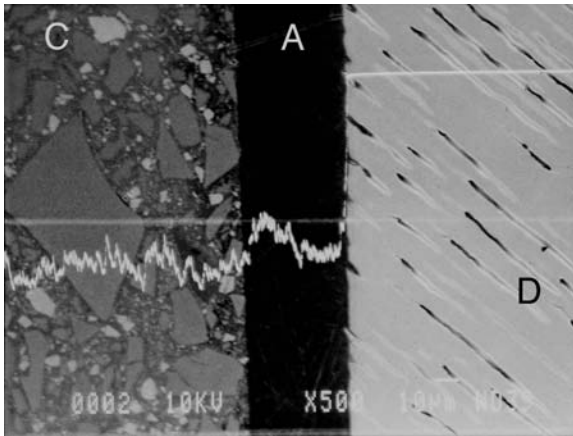
using silicon carbide paper (240, 600 and 1000 grit) and diamond pastes (6, 3 and 1 μm). Between each polishing step using diamond pastes, the specimens are rinsed with running tap water and ultrasonically cleaned for 1 min in order to remove remnants of polishing debris and pastes. After polishing or fracturing, the specimens are subjected to overnight fixing in 2.5% glutaraldehyde in 0.1M sodium cacodylate buffer (0.1M, pH 7.4) or 10% neutral buffered formalin. When imaging the tooth/resin interface using argon ion beam bombardment (Fig. 3.11), the bombardment should be performed after fixation (Harnirattisai *et al.*, 1992, 1993; Van Meerbeek *et al.*, 1992; Inokoshi *et al.*, 1993). For dehydration, the fixed specimens are subjected to ascending grades of ethanol (50%, 75%, 95% and 100%) followed by critical point drying (CPD), HMDS drying or freeze drying (FD) (Pashley *et al.*, 1993; Perdigao *et al.*, 1995, 1996). The dried specimens are then sputter coated for SEM observation.

3.2.5 Energy-dispersive x-ray spectroscopy (EDS or EDX)

Energy-dispersive x-ray spectroscopy (EDS or EDX) is an analytical tool predominantly used for chemical characterization. A focused electron beam interacts with the atoms in a sample. Characteristic x-ray photons are



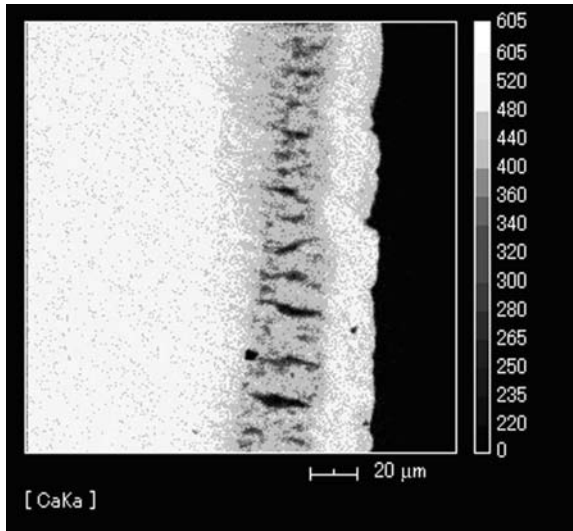
3.11 SEM image of an argon ion etched resin/dentine interface. The specimen was highly polished with diamond pastes followed by argon ion etching treatment. Then, the specimen was gold coated and observed using FE-SEM. The hybrid layer (H) is clearly observed between the cured adhesive resin (A) and the underlying mineralized dentine (D).



3.12 Line scanning mode of calcium analysis using EDS. The specimen was highly polished with diamond pastes and sputtered with gold (generally carbon coating is used but the peak of $\text{CaK}\alpha$ does not overlap with the peak of gold; gold coating gives better image contrast when compared with carbon coating). Scanning was performed across the resin composite (C), cured adhesive resin (A) and dentine (D). The image was made using backscattered mode detection because this enhances the elemental or density differences at the specimen surface (atomic number contrast).

generated by this interaction. The energy levels of the characteristic x-rays are different among elements (Lee *et al.*, 2004; Petridis *et al.*, 2004; Otulakowska and Nicholson, 2006).

In our field, EDS is generally used for elemental analysis. The characteristic feature of EDS is its multiple channel analysis which enables analysis of a wide range of elements at the same time. EDS may be used to allow microanalysis of which elements are present in a sample. Line scanning (Fig. 3.12) and elemental mapping to determine (Fig. 3.13) are also widely used in our field. Figure 3.12 shows the calcium line scan through a resin dentine interface superimposed upon a backscattered electron image. The concentration of calcium appeared to be very low within the resin composite (C) and gradually showed a slight increase within the cured adhesive resin (A). Subsequently, the calcium concentration plateaus within the dentine (D). Figure 3.13 shows calcium mapping of cross-cut human enamel that has been subjected to a demineralization and re-mineralization cycle. The brighter parts of the image represent higher concentrations of calcium. The darker areas show the regions of low calcium concentration which represents the subsurface demineralization of superficial enamel.



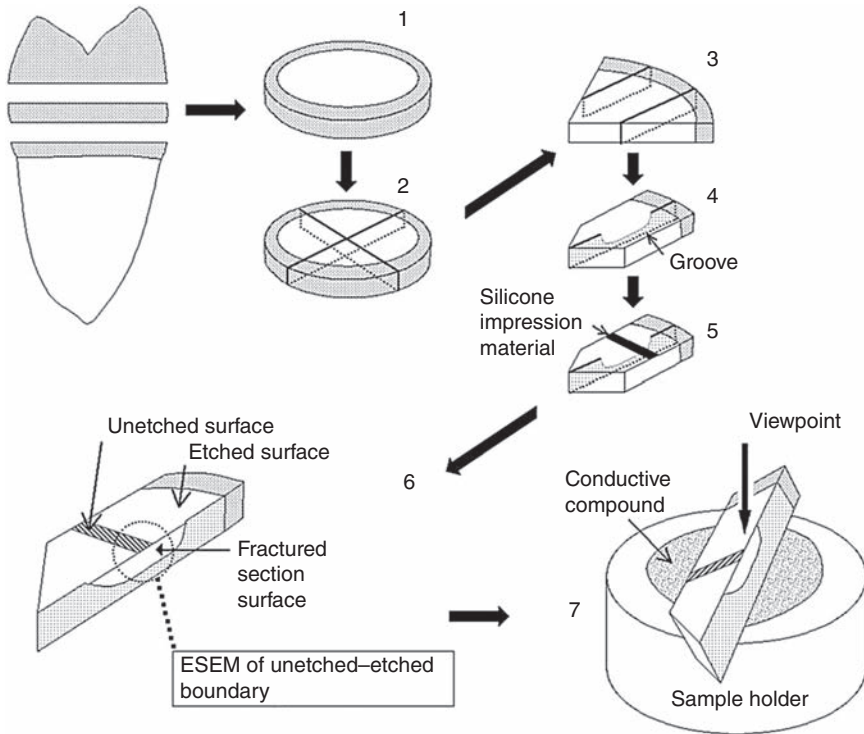
3.13 Calcium mapping image of enamel using EDX (the original photograph was a full color image). The different concentrations of calcium can be evaluated qualitatively using the color bar, on the right.

3.2.6 Wavelength-dispersive x-ray spectrometer

The emission of characteristic x-rays in an SEM chamber for wavelength-dispersive x-ray spectroscopy (WDS) is caused by the same mechanisms as EDS. Because the wavelengths of these x-rays are characteristic of the emitting species, the sample composition can be easily identified by recording WDS spectra. Wavelength-dispersive x-ray spectrometers are based on Bragg's law and use various moveable, shaped monocrystals as monochromators (Hals *et al.*, 1988; Ferracane *et al.*, 1998; Lim *et al.*, 2003). In other words, WDS can be described as a single-channel micro-analyzer. Although spectral resolution and detector dead time of WDS are much better than EDS, when compared with EDS, WDS requires a flat specimen surface and time-consuming procedures for multiple elemental analysis of the specimen. Thus, EDS is perhaps a more useful tool for biomaterials research.

3.2.7 Environmental scanning electron microscope (ESEM)

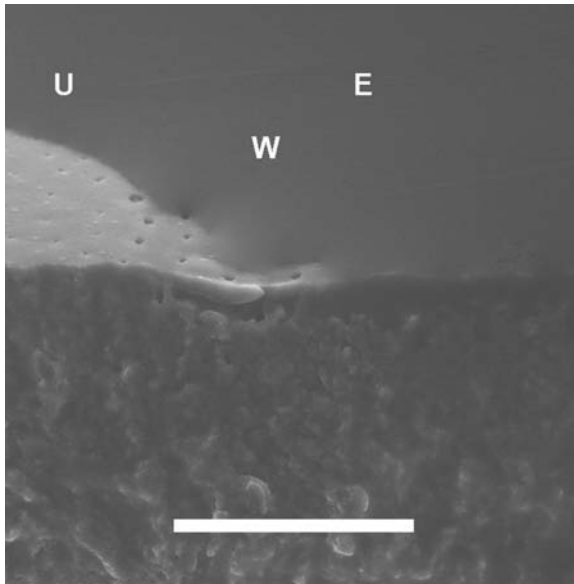
An environmental scanning electron microscope (ESEM) permits the imaging of wet systems with no prior specimen preparation (Inokoshi *et al.*, 1996; de Wet *et al.*, 2000; Idriss *et al.*, 2003; Bergmans *et al.*, 2005). When



3.14 Schematic drawing of specimen preparation for ESEM. Courtesy of Dr. S. Inokoshi.

using an ESEM, the sample environment can be dynamically altered. As vapor is tolerated in the sample chamber, the ESEM makes it possible to carry out wet imaging of samples. In order to view a wet sample, the atmosphere in the sample chamber must be carefully controlled at all stages. After the sample is placed in the chamber, air at atmospheric pressure must be replaced by water vapor at a few torr. It is important to carry out the pump-down carefully so that premature dehydration of the dispersion does not occur (Stokes, 2003; Muscariello *et al.*, 2005).

Figure 3.14 shows an example of specimen preparation for ESEM observation. A dentine disk without enamel remnants and pulp exposure was cut from the coronal part of each tooth with a diamond saw microtome (Fig. 3.14, stage 1). The section surface was polished with wet silicon carbide papers and diamond pastes. Each disk was further cut into quarters, producing four samples (Fig. 3.14, stage 2). The lateral edges of each quarter were trimmed (Fig. 3.14, stage 3). A groove was cut on the bottom surface extending to the polished top surface, excluding the central region of the sample, by means of a 0.15mm thick diamond disk. Addition-type silicone

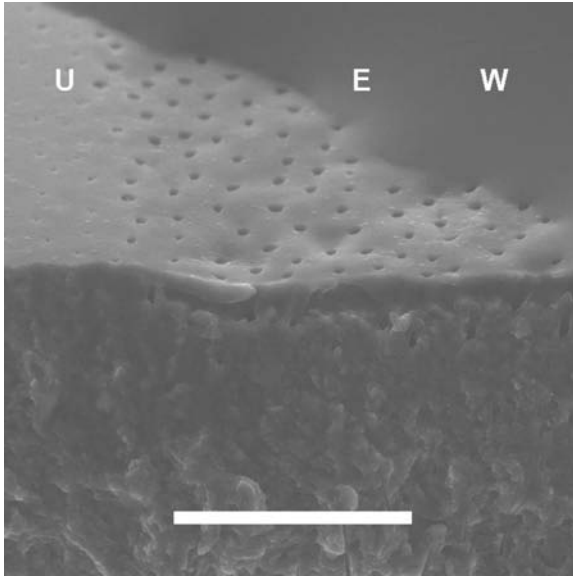


3.15 ESEM image of wet demineralized and mineralized dentine. All images (Figs 3.9 to 3.11) were taken at 5 Torr and 5°C. (U, unetched dentine; E, etched dentine; W, water. Scale bar, 50µm.) Courtesy of Dr. S. Inokoshi.

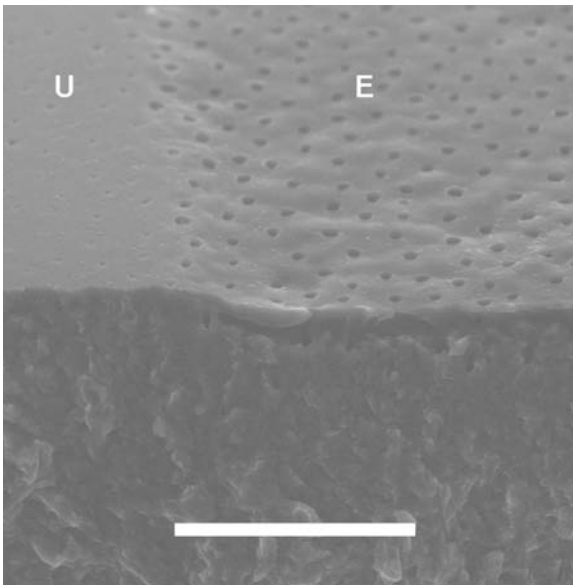
impression material was mixed and a string of the material was placed on the polished surface, so as to produce a reference surface without acid conditioning, as shown in Fig. 3.14, stage 5.

Acid etching was applied to the surface for 60s, followed by rinsing with running tap water for 15s. The string of impression material covering the surface was then carefully removed with sharp-pointed tweezers taking care not to damage the underlying surface. Small scissors were used to fracture the sample into two pieces by applying force along the groove (Fig. 3.14, stage 6). The fractured sample was fixed with conductive compound tilted on a sample holder, in order to view both top and fractured surfaces of the etched and unetched boundary simultaneously (Fig. 3.14, stage 7). A small amount of distilled water was supplied with a syringe to cover the sample with water, in order to prevent the sample from dehydrating before observation. The samples were then observed within the ESEM chamber.

Figure 3.15 shows the wet etched (E) and unetched dentine (U) taken at 5 Torr and 5°C. Most of the etched dentine is covered with water (W) which shows as a flat and amorphous image. Some of the tubule apertures are visible on the etched dentine that is very close to the unetched dentine. As water evaporates, the region covered with water shows recession toward



3.16 ESEM image of slightly dried demineralized and mineralized dentine. (U, unetched dentine; E, etched dentine; W, water. Scale bar, 50 μm .) Courtesy of Dr. S. Inokoshi.



3.17 ESEM image of dried demineralized and mineralized dentine. (U, un-etched dentine; E, etched dentine; W, water. Scale bar, 50 μm .) Courtesy of Dr. S. Inokoshi.

the right side of the image on the demineralized dentine surface, showing the increased numbers and diameters of the tubule apertures (Fig. 3.16). Figure 3.17 shows complete evaporation of water on the etched surface. Unetched (U) and etched (E) dentine are clearly distinguished. Unetched dentine shows as a flat surface with complete closure of the dentinal tubules by smear plugs. The etched dentine surface appears to be collapsed because of progressive dehydration, with larger tubular openings. The ESEM enables us to observe water-containing specimens without coating or inducing other artifacts. Moreover, it is possible to observe a wet restoration/tooth interface and then to remove the residual water and observe dehydration effects.

3.3 Summary

EM imaging of specimens is indispensable in the biomaterials research field. Increasing development of new techniques and/or materials requires proper evaluation of both the techniques and the materials. Despite many new developments, the nature of the interactions between restorations and the tooth interface is still unclear. Mechanical and chemical testing helps us to speculate about the interactions between the restoration and tooth. However, without thorough EM imaging of the restoration/tooth interface, it would be difficult to obtain a good understanding of this important structure. The specialized nature of EM equipment and the specialized techniques needed for its implementation as well as the associated significant expense may place it out of reach for a single research institute. Collaboration between institutes makes it possible to share these techniques and equipment for pioneering research projects. To reiterate, transmission and scanning electron microscopy related analytical techniques are very useful for disclosing the interactions between restorations and the tooth interface. The skill of the researcher is based upon choosing the correct analytical technique or methods to avoid inherent limitations, artifacts and errors when undertaking such research projects.

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Dental adhesives and adhesive performance

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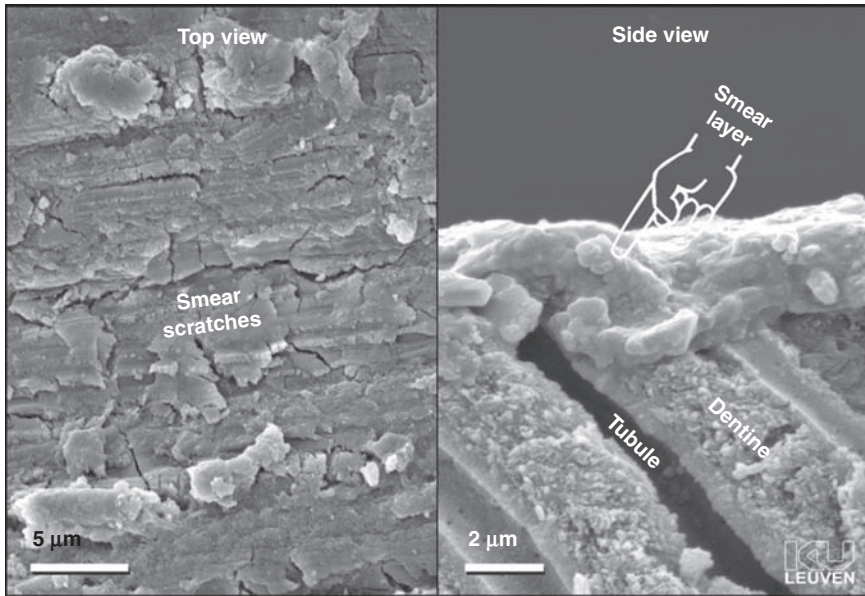
4.1 Introduction

The use of composite filling materials along with adhesive techniques has revolutionized today's dental practice. The esthetic potential, handling and wear properties of composite fillings have improved tremendously.¹ In the hands of a skillful dentist, composite fillings today are able to replace lost tooth tissue in an invisible way. However, no matter how splendid the shape and color, a good composite filling does not last long without a good bond to the remaining tooth structure.

Basically, the main bonding mechanism of current adhesives can be regarded as an exchange process involving substitution of inorganic tooth material by resin monomers that upon *in situ* setting become micro-mechanically interlocked in the created micro-porosities.² Diffusion is the primary mechanism to obtain such micro-mechanical retention. Recently, more evidence has corroborated the potentially important role of additional chemical interactions at the biomaterial–tooth interface, especially with regard to bond stability.^{3,4} In this chapter, the current status – circa 2007 – regarding bonding of dental adhesives to enamel and dentine is reviewed.

4.2 The smear layer as an 'obstacle' to bonding

Cavity preparation alters the uppermost layer of tooth tissue, covering the tooth surface with a smear layer. While cutting dentine, the heat and shear forces produced by the rotary movement of the bur cause dentine debris to compact and aggregate. The resultant smear layer is an adherent layer of debris and is revealed by scanning electron microscopy (SEM) as a 1–2 μm layer of debris with a mainly granular substructure that entirely covers dentine (Fig. 4.1).⁵ The orifices of the dentine tubules



4.1 Field-emission-gun (FEG)-SEM photomicrographs of a smear layer produced by a diamond bur on dentine.

are obstructed by debris tags, called smear plugs, that are contiguous with the smear layer and may extend into the tubules to a depth of 1–10 μm .⁶ The smear layer consists of shattered and crushed hydroxyapatite, as well as fragmented and denatured collagen that in clinical conditions may also be contaminated by bacteria and saliva. Early non-acidic adhesives failed, as they did not penetrate profoundly enough to establish a bond with intact dentine. In order to overcome this ‘smear-layer’ obstacle, a certain degree of etching is consequently required. There are basically two options, i.e. removal of the smear layer before bonding or the use of adhesives that can penetrate beyond the smear layer while incorporating it.⁷ The first adhesives achieving clinically acceptable results were based on smear-layer removal, and are known as ‘etch&rinse’ adhesives.⁸ More recently, smear-layer incorporating or ‘self-etch’ adhesives have become popular, especially because of their ease of use and faster application procedure (Table 4.1).⁸ Some of those self-etch adhesives interact very superficially with the smear layer and the underlying dentine. In addition to the shallow micro-mechanical interlocking, they can also chemically interact with residual hydroxyapatite following a two-fold bonding mechanism similar to that of glass ionomers. The latter glass-ionomer bonding strategy can be regarded as a third strategy to achieve bonding to tooth tissue.⁸

Table 4.1 Overview of currently available adhesives categorized according to the classification of Van Meerbeek *et al.*⁸

Adhesive	Manufacturer
Three-step etch&rinse adhesives (3-E&R)	
Adper Scotchbond Multi-Purpose	3M ESPE, Seefeld, Germany
Adper Scotchbond Multi-Purpose Plus	3M ESPE
All-Bond 2	Bisco Inc., Schaumburg, IL, USA
All-Bond 3	Bisco
Bond-it	Pentron Corporation, Wallingford, CT, USA
Clearfil Liner Bond	Kuraray Medical Inc., Tokyo, Japan
cmf Adhesive System	Saremco, Rebstein, Switzerland
Ecusit-Primer/Mono	DMG, Hamburg, Germany
Gluma Solid Bond	Heraeus Kulzer, Hanau, Germany
Optibond	Kerr, Orange, CA, USA
Optibond FL	Kerr
PAAMA 2	SDI Limited, Bayswater, Victoria, Australia
PermaQuick	Ultradent, South Jordan, UT, USA
ProBond	Dentsply, Kontanz, Germany
Quadrant Unibond	Cavex Holland B.V., Haarlem, the Netherlands
Solobond Plus	VOCO, Cuxhaven, Germany
Syntac	Ivoclar Vivadent, Schaan, Liechtenstein
Two-step etch&rinse adhesives (2-E&R)	
Adper Scotchbond 1 XT Adhesive (Single Bond Plus)	3M ESPE
Bond-1	Pentron Corporation
Clearfil Photobond	Kuraray Medical Inc.
Clearfil New Bond	Kuraray Medical Inc.
Excite	Ivoclar Vivadent
Excite DSC	Ivoclar Vivadent
Gluma Comfort Bond	Heraeus Kulzer
Gluma One Bond	Heraeus Kulzer
Go!	SDI Limited
Heliobond	Ivoclar Vivadent
One Coat Bond	Coltene-Whaledent, Altstätten, Switzerland
One-Step	Bisco Inc.
One-Step Plus	Bisco Inc.
Optibond Solo Plus	Kerr
Optibond Solo Plus Dual Cure	Kerr
Peak LC Bond	Ultradent
Polibond	VOCO
Prime&Bond NT	Dentsply
Prime&Bond NT dual cure	Dentsply
PQ1	Ultradent
Quadrant Uni-1-Bond	Cavex Holland B.V.
Solist	DMG
Solobond M	VOCO
Stae	SDI Limited
Superbond C&B	Sun Medical Co., Shiga, Japan

Table 4.1 Continued

Adhesive	Manufacturer
TECO	DMG
XP BOND	Dentsply
Two-step self-etch adhesives (2-SEA)	
AdheSE	Ivoclar Vivadent
Adper Scotchbond SE	3M ESPE
All-Bond SE (including All-Bond SE Liner)	Bisco Inc.
Clearfil Liner Bond 2 (Clearfil Liner Bond II in Japan)	Kuraray Medical Inc.
Clearfil Liner Bond 2V (Clearfil Liner Bond II Σ in Japan)	Kuraray Medical Inc.
Clearfil Protect Bond	Kuraray Medical Inc.
Clearfil SE Bond (Clearfil Mega Bond in Japan)	Kuraray Medical Inc.
Contax	DMG
FL Bond (Imperva Fluorobond in Japan)	Shofu Inc., Kyoto, Japan
Frog	SDI Limited
Microbond/Microbond Duo	Saremco
Nano-Bond	Pentron Corporation
One Coat Self Etching Bond	Coltene-Whaledent
Optibond Solo Plus Self-etch	Kerr
One-step Plus/Tyrian SPE	Bisco Inc.
Peak Self-Etch	Ultradent
Tokuso Mac Bond II	Tokuyama Dental Corporation, Tokyo, Japan
Unifil Bond	GC, Tokyo, Japan
One-step self-etch adhesives (1-SEA)	
Absolute 2	Dentsply
AdheSE One	Ivoclar Vivadent
Admira Bond	VOCO
Adper Easy Bond	3M ESPE
Adper Prompt L-Pop	3M ESPE
All-Bond SE	Bisco Inc.
AQ Bond (also Touch&Bond by Parkell, USA)	Sun Medical Co.
Bond Force	Tokuyama Dental Corporation
Clearfil S ³ Bond	Kuraray Medical Inc.
Futurabond NR	VOCO
G-Bond	GC
Hybrid Bond	Sun Medical Co.
iBond	Heraeus Kulzer
James-2	Saremco
OptiBond All-In-One	Kerr
One-up F Bond	Tokuyama Dental Corporation
One-up Bond F Plus	Tokuyama Dental Corporation
Reactmer Bond	Shofu Inc.
Tyrian SPE	Bisco Inc.
Xeno III (Xeno CF II in Japan)	Dentsply
Xeno IV	Dentsply
Xeno V	Dentsply

For more information with regard to composition and pH, see Van Landuyt *et al.*⁷⁶

4.3 The hybridization process

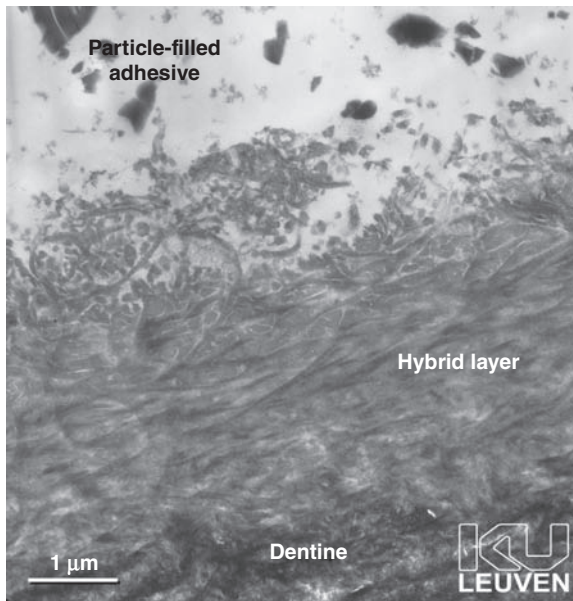
Micro-morphological characterization of the interface is paramount to gain insight into the bonding mechanism to tooth tissue. As the adhesive interaction process occurs over a couple of micrometers, electron microscopy is preferred on grounds of the high resolution that can be achieved (see Chapter 3 in this volume). In particular, the transmission electron microscope (TEM) provides highly informative images of both the interaction zone with intact dentine and that with the resin layers.

All categories of adhesives exhibit the common adhesion mechanism of hybridization. This is the process of micromechanical interlocking ensuing a demineralization, infiltration and polymer setting process, and was first described by Nakabayashi *et al.*⁹ A hybrid layer is the resulting resin-infiltrated surface layer of dentine (and enamel).

4.3.1 Etch&rinse adhesives

Etch&rinse adhesives can readily be recognized by an initial etching step, the so-called ‘conditioning step’, followed by a compulsory rinsing phase. Another frequently used name for this category of adhesives is ‘total-etch’ adhesives; this is, however, less appropriate because self-etch adhesives also etch and demineralize tooth tissue, and are also applied simultaneously to enamel and dentine.^{8,10,11} This etching step produces etch pits within the enamel, and demineralizes dentine in order to remove the smear layer and smear plugs, and so achieves a micro-porous surface with enhanced bonding receptiveness.

Originally, three-step etch&rinse systems typically consisted of three separate application steps: (a) conditioning, (b) priming and (c) adhesive resin application. In the search for fewer application steps and simplification, a two-step etch&rinse approach combines the priming and bonding steps into one; these adhesives are frequently referred to as ‘one-bottle adhesives’ and misleadingly suggest a single application step. Both three- and two-step etch&rinse adhesives pursue a similar adhesion mechanism. In the conditioning step, phosphoric acid removes the smear layer while concurrently demineralizing dentine over a depth of 3–5µm, thereby exposing a scaffold of collagen fibrils that is nearly totally depleted of hydroxyapatite.^{12,13} The exposed collagen fibrils function as a micro-retentive network for micro-mechanical interlocking of resin monomers that diffuse into it and polymerize *in situ*, eventually forming the so-called hybrid layer (Fig. 4.2). Hydroxy ethyl methacrylate (HEMA) is often one of the key components for this type of adhesive. Infiltration of the thick (3–5µm) and potentially collapsed demineralized collagen network requires very hydrophilic and low molecular weight monomers such as

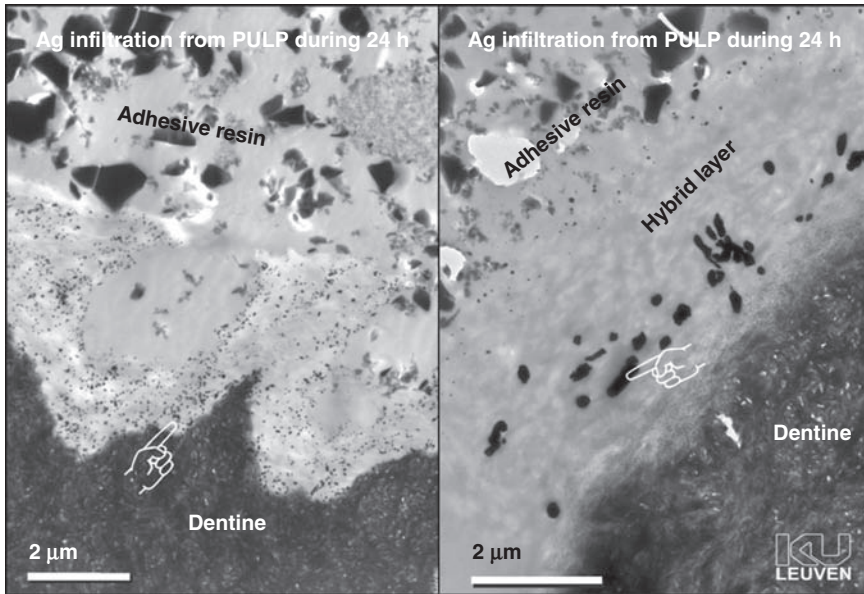


4.2 TEM photomicrograph of the adhesive–dentine interface produced by the three-step etch&rinse adhesive cmf adhesive system (Saremco).

HEMA. The re-expansion of the collagen mesh that has collapsed upon post-conditioning air-drying¹⁴ is especially crucial for bond strength improvement.¹⁵

Neither the thickness of the hybrid layer, nor the length of the resin tags seem to play an important role regarding the bond strength.^{16,17} True chemical adhesion between collagen and the methacrylate monomers is unlikely, because of the inert nature of collagen fibrils and the low affinity of the monomers for hydroxyapatite-depleted collagen.¹⁸ Consequently, the rather poor adaptation of resin to the collagen fibrils leaves nanometer-sized gaps that have been shown to absorb silver (Fig. 4.3 and Chapters 2, 3 and 5 of this volume), representing the so-called ‘nano-leakage’ phenomena.¹⁹ This process is thought to be primarily responsible for the gradual degradation of the bond.^{20,21}

Bonding to enamel is still today best accomplished using this etch&rinse approach. A 35% phosphoric acid etch&rinse phase removes the enamel top layer for a few micrometers, and selectively dissolves hydroxyapatite crystals within prismatic and interprismatic enamel.²² This increases microscopic roughness, surface area and surface energy. The simple application of a hydrophobic low-viscosity resin or ordinary bonding agent efficiently infiltrates the etch pits by capillary attraction. Upon *in situ* polymerization micro- and macro-tags are formed that are responsible for the durable

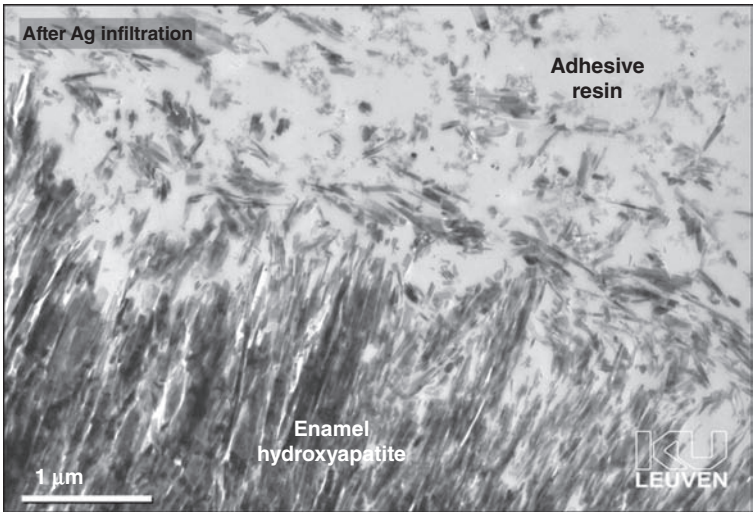


4.3 Examples of nano-leakage that became observable by immersion of the specimens in silver nitrate and eventually by TEM imaging.

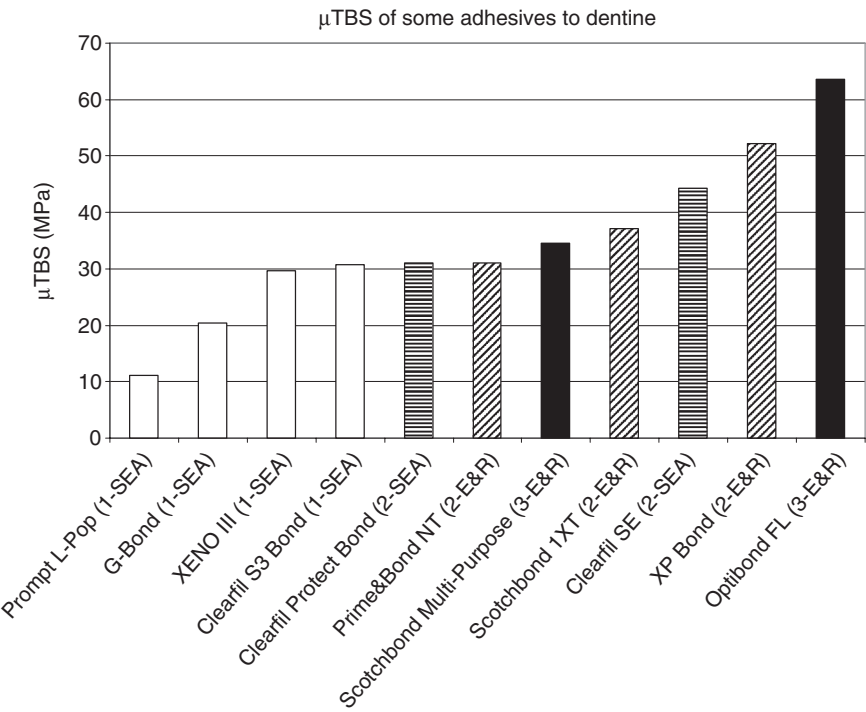
micro-mechanical interlocking at the enamel achieved following this etch&rinse procedure (Fig. 4.4). This bond to enamel not only effectively seals the restoration margin, but even protects the more vulnerable bond to dentine against degradation.²¹

So far, *in vitro* and *in vivo* research has indicated that etch&rinse adhesives can achieve high-quality adhesion to both enamel and dentine (Fig. 4.5).^{2,8,23,24} In laboratory and clinical studies, the performance of three-step etch&rinse adhesives is commonly superior to that of two-step etch&rinse adhesives.^{16,23,25,26} The latter are also associated with greater technique sensitivity than their three-steps counterparts, which is understandable as a single solution combines the two separate functions of primer and bonding resin.²⁷ Moreover, after aging procedures in durability studies, the bonding integrity of three-step etch&rinse adhesives is better maintained.^{21,28} Therefore, three-step etch&rinse adhesives are still today considered as the ‘gold standard’ among adhesives, in spite of the rather elaborate and lengthy working procedure.

The primer solvent within etch&rinse adhesives is a major factor affecting the handling²⁹ and performance¹⁵ properties of etch&rinse adhesives. Water-based adhesives are believed to be the most forgiving regarding application errors, but the water content in the resultant interface jeopardizes the durability. Acetone-based adhesives on the other hand have



4.4 TEM photomicrograph of the adhesive–enamel interface produced after an etch&rinse procedure (OptiBond FL, Kerr). The sample has been immersed in a silver nitrate solution to check for nano-leakage. No deposits of silver (black dots) can be observed, suggesting that the interface is adequately sealed.



4.5 Micro-tensile bond strength (μTBS) of some of today’s adhesives to dentine, measured following the Leuven μTBS protocol.

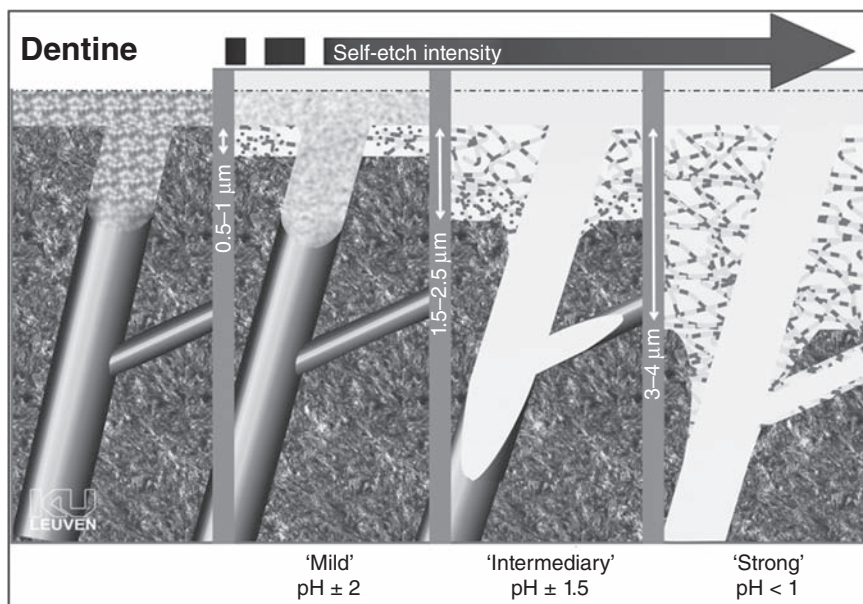
water-free formulations, but require the challenging ‘wet-bonding’ technique.^{29,30} Ethanol-based adhesives are believed to be a good compromise with regard to user-handling and performance.⁸ One of the most recent new developments with regard to etch&rinse adhesives was the use of ter-butanol in the recent two-step etch&rinse adhesive XP-Bond (Dentsply) (Table 4.1). Ter-butanol is a solvent with a similar vapor pressure to ethanol, but with a better capability for chemical reaction with monomers. This new etch&rinse adhesive has recently shown good micro-tensile bond strength data (Fig. 4.5), as well as performed well when tested following a conventional shear bond strength test by general practitioners in the so-called ‘Battle of the adhesives’ series by Degrange *et al.*³¹

4.3.2 Self-etch adhesives

Although the self-etch concept is not new,² it has only in the last five years come under extensive scrutiny. First, self-etch adhesives were developed by raising the amount of acidic monomers in HEMA–water-based adhesives.¹⁰ Self-etch adhesives do not require a separate ‘etch&rinse’ phase, as they contain acidic monomers that simultaneously condition and prime enamel and dentine. As a result, the dissolved smear layer and demineralization products are not rinsed away, but incorporated in the adhesive resin.^{32,33}

Self-etch adhesives can be subdivided according to the number of application steps, and their acidity (pH) and resultant etching aggressiveness (Fig. 4.6).^{2,34} Similarly to etch&rinse adhesives, a two-step and a simplified one-step version of self-etch adhesives or so-called ‘all-in-one’ adhesives exist.³⁵

The morphological features of the hybrid layer produced by self-etch adhesives depend a great deal on the aggressiveness of the functional monomers.^{8,36} Consequently, three categories of self-etch adhesives can be described according to their acidity: mild ($\text{pH} \geq 2$), intermediate ($\text{pH} \approx 1.5$) and strong self-etch adhesives ($\text{pH} \leq 1$) (Figs 4.6 and 4.7).^{34,37} ‘Mild’ self-etch adhesives demineralize dentine only very shallowly, forming a rather shallow hybrid layer with submicron dimensions, while leaving hydroxyapatite crystals around the collagen fibrils (Fig. 4.8). TEM images of ‘strong’ self-etch adhesives applied on dentine strongly resemble the morphological aspect of an etch&rinse adhesive with a thick hybrid layer, which is completely devoid of hydroxyapatite crystals, and with resin tags (Fig. 4.7; left). The more aggressive the adhesive, the deeper the hybridization.³⁸ ‘Intermediary strong’ self-etch adhesives exhibit morphological features that lie between the ‘mild’ and ‘strong’ self-etch adhesives. Apart from the pH of the self-etch solution, other factors such as agitation during application, thickness of the smear layer, viscosity and wetting characteristics also account for



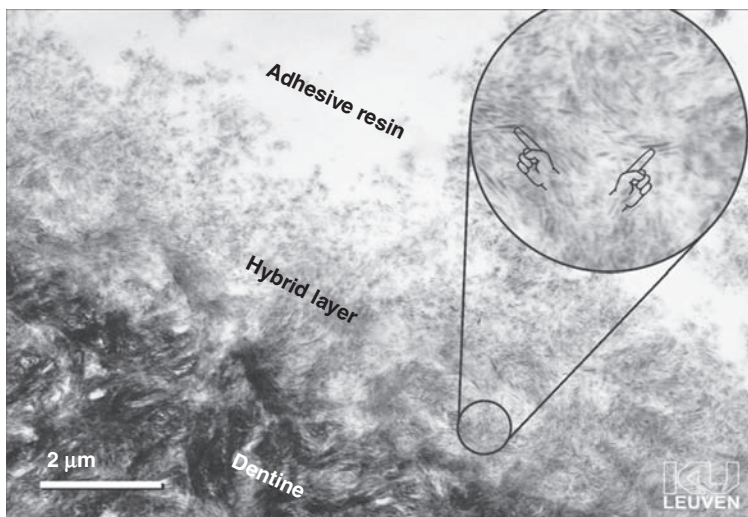
4.6 Schematic demonstrating the difference in interfacial ultrastructure depending on the pH of the self-etch adhesive. The black dots represent residual hydroxyapatite.

the resultant depth of infiltration and demineralization by self-etch adhesives.^{39,40}

In spite of the small hybrid layer and the absence of resin tags (little micro-mechanical retention), 'mild' self-etch adhesives such as Clearfil SE (Kuraray) can reach satisfactory results as far as bond strength is concerned (Fig 4.5).^{8,16} Together with the finding that the thickness of the hybrid layer and the presence of resin tags do not overly influence the bonding performance,^{16,17} additional chemical interaction between the monomers and hydroxyapatite may be a plausible explanation for the good performance of some self-etch adhesives.⁴ One has to keep in mind that the interaction of self-etch adhesives with tooth substrate is dependent to a great extent on the kind of acidic functional monomer and eventually the overall composition of the adhesive. This results generally in a larger variation in bonding performance of the different self-etch adhesives available today than of the etch&rinse adhesives that all rely largely on the use of phosphoric acid and the subsequent infiltration of monomers. The carboxylic and phosphate groups that render these monomers hydrophilic and that function as proton donors, have been proven to bond ionically with calcium in hydroxyapatite.⁴¹ Figure 4.9 shows some

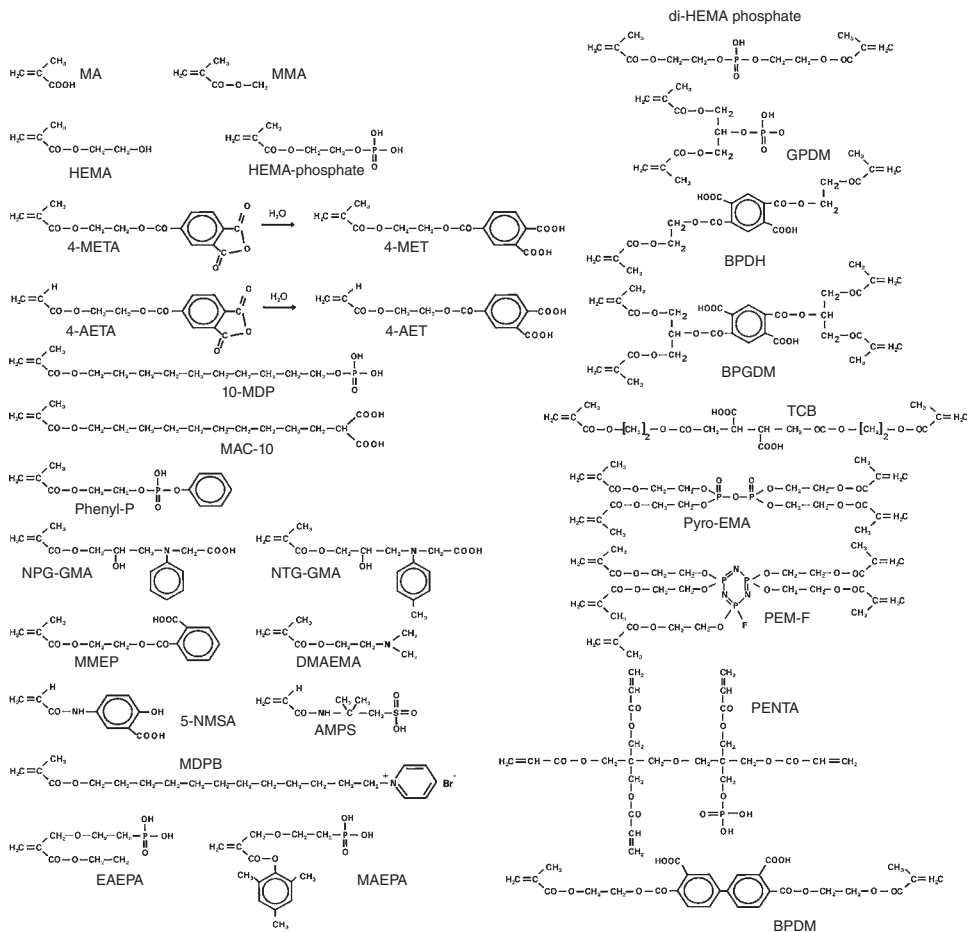


4.7 TEM photomicrographs showing the adhesive–dentine interface produced by, respectively, a 'strong' self-etch adhesive (left-hand-side, Adper Prompt L-Pop, 3M ESPE) and a 'mild' self-etch adhesive (right-hand-side, Clearfil SE, Kuraray). Note the markedly different interfacial ultrastructure with the formation of a deep (left) versus only a shallow (right) hybrid layer. Only in the latter does hydroxyapatite (HAp) still remain.



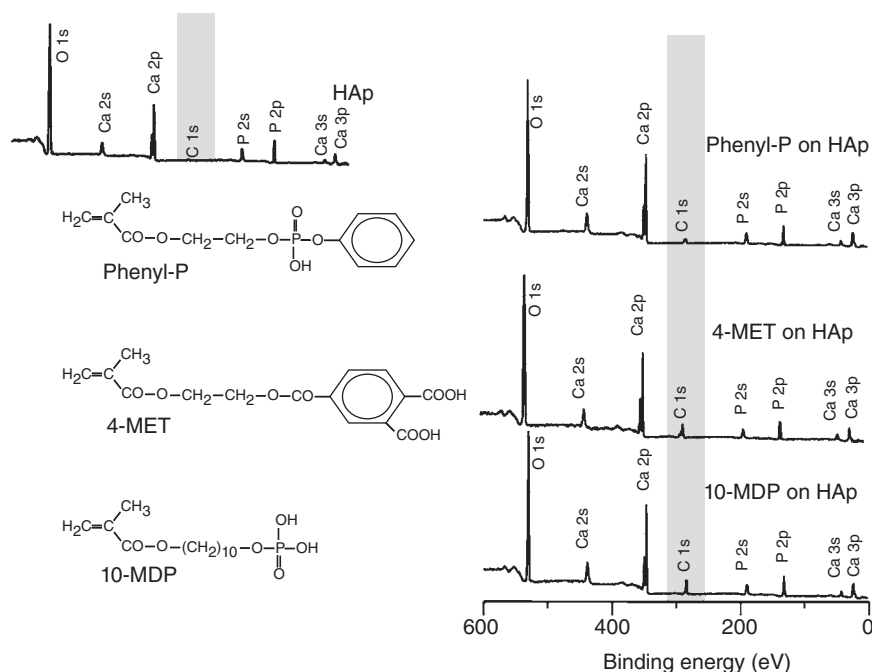
4.8 TEM photomicrograph illustrating the adhesive–dentin interface produced by a mild self-etch adhesive. The hybrid layer of about $1 \mu\text{m}$ thickness still contains residual hydroxyapatite (shown in inset) that serves as receptor for chemical interaction with the adhesive's functional monomer.

Functional monomers



4.9 Overview of functional monomers used in current self-etch adhesives.

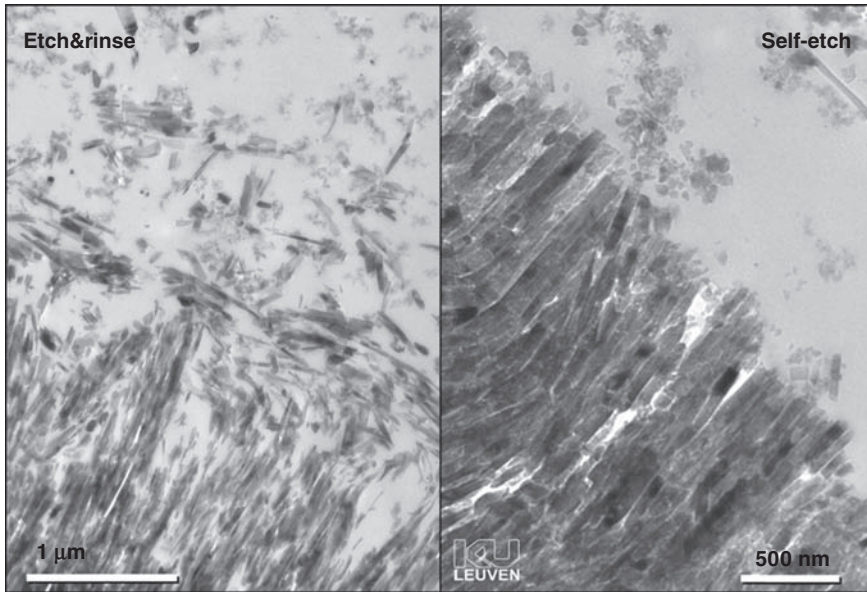
polycarboxyl- and phosphate-based monomers, as typically used in self-etch adhesives. The ability to bond chemically is monomer-specific and depends on the hydrolytic stability of the calcium–monomer bond. Using x-ray photoelectron spectroscopy (XPS), Yoshida *et al.*⁴ have shown that 10-MDP (10-methacryloxydecyl dihydrogen phosphate) exceeds the bonding potential of 4-MET (4-methacryloxyethyl trimellitic acid) and phenyl-P (2-methacryloxyethyl phenyl hydrogen phosphate) (Fig. 4.10). The hydrolytic stability of the monomer itself is also important, especially with regard to bond durability. Whereas micro-mechanical retention is



4.10 X-ray photoelectron spectroscopy (XPS) of the chemical interaction of three functional monomers with synthetic HAP. The significantly most intense C 1s peak was recorded for 10-MDP, suggesting the most intense chemical interaction with HAP through ionic bond formation.

thought to provide resistance to ‘acute’ de-bonding stresses, the relevance of additional chemical bonding is suggested to lie in durability and survival of adhesion.^{2,8}

The composition of self-etch adhesives is unusual in that they contain high concentrations of water and acidic monomers.³⁶ Water is an indispensable ingredient of current self-etch systems; it provides an ionization medium for the functional monomers.⁴² Two-step self-etch adhesives consist of a hydrophilic aqueous primer solution and a separate hydrophobic adhesive resin. Similar to the combined primer–adhesive resin solution of two-step etch&rinse adhesives, one-step self-etch adhesives are complex mixtures of both hydrophilic and hydrophobic components. In particular, the high concentrations of water have raised questions about potentially harmful effects on polymerization, given that complete water removal is unrealistic.^{42,43} This also applies to the high concentrations of solvent that may cause incomplete resin polymerization in case of incomplete evaporation.



4.11 TEM photomicrographs showing the enamel–adhesive interface produced by, respectively, an etch&rinse adhesive (left panel, OptiBond FL, Kerr) and a ‘mild’ self-etch adhesive (right panel, Clearfil SE, Kuraray). Note the markedly different interfacial ultra-structure with deep (left) versus only shallow (right) resin tags.

When bonding to enamel, the ‘strong’ self-etch adhesives, in general, perform better than the higher pH self-etch adhesives.⁸ Nevertheless, with some ‘mild’ self-etch adhesives such as Clearfil SE (Kuraray), a quite high and stable bond strength is achieved, which must most likely be attributed to the good chemical interaction potential of the functional monomer (10-MDP in Clearfil SE, Kuraray). Ultrastructurally, the interaction with enamel is very shallow with the sole formation of micro-tags only (Fig. 4.11).

While bonding to enamel may remain a problem, especially for ‘mild’ self-etch adhesives,^{25,40} bonding to dentine has given results similar to those obtained by the gold-standard three-step etch&rinse adhesives.¹⁶ Recent studies have also reported good clinical results for some self-etch adhesives. Clearfil SE (Kuraray), which is a ‘mild’, two-step self-etch adhesive, was reported to have high retention rates in non-carious class V cavities after, respectively, 5 and 2 years.^{44,45}

Compared with etch&rinse adhesives, many advantages have been attributed to self-etch adhesives. It has been suggested that they improve the efficiency in clinical procedures by omitting the obligatory rinse phase in

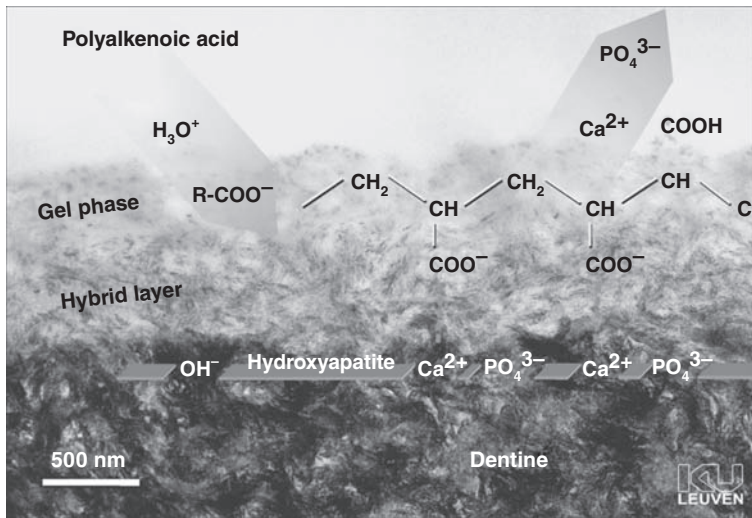
etch&rinse adhesives and thus reducing the chairside time.⁴⁶ Conditioning, rinsing and drying steps, which may be critical and difficult to standardize in clinical conditions, are eliminated in self-etch adhesives.⁴⁰ Technique sensitivity associated with bonding to dehydrated demineralized dentine is eliminated, as rinsing and drying phases are no longer needed.⁴⁷ Collapse of the collagen network is prevented, as monomers infiltrate concomitantly as they demineralize.^{22,23,48} Theoretically, incomplete resin infiltration is prevented in this way as well.^{33,36} However, recent nano-leakage observations in the hybrid layer, and especially beyond the hybrid layer, have shed doubt on the concept that self-etch adhesives ensure complete resin infiltration.⁴⁹ As the smear layer and smear plugs are not removed before the actual bonding procedure, rewetting of dentine by dentinal fluid from the dentine tubules is prevented⁵⁰ and potential postoperative sensitivity has been reported to be reduced.^{42,51} Perdigão *et al.*,⁵² however, could not observe any difference in postoperative sensitivity between a three-step etch&rinse adhesive and a self-etch system.

4.3.3 Glass-ionomer approach

The third adhesive approach is based on the technology of glass ionomers and their auto-adhesive capacity. Glass ionomers are the only true self-adhesive materials as they can adhere to both enamel and dentine by a specific glass-ionomer interaction. Diverse formulae of glass ionomers are on the market, varying in their uses: glass-ionomer restorative materials, cements and even adhesives to bond composites to tooth tissue.

Glass ionomers have a specific composition, containing polyacrylic acid, alkenoic copolymers, glass-filler particles and water. When resin components are added to glass ionomers, these are called 'resin-modified glass ionomers'. The adhesion reaction to tooth tissue is mainly based on the glass-ionomer components and involves both a micro-mechanical hybridization and a chemical reaction. In the particular case of glass-ionomer adhesives, which are actually resin-modified glass ionomers, the resin components ensure good bonding with the lining composite.

Regarding bonding mechanism, glass ionomers can be considered a special group of self-etch adhesives based on glass-ionomer technology. Like self-etch adhesives, their mechanism of adhesion is two-fold and depends both on a limited demineralization of enamel and dentine with subsequent infiltration and mechanical interlocking, and on a chemical adhesion between calcium in hydroxyapatite and polyalkenoic acid (PAA) (Fig. 4.12).^{41,53,54} The demineralization reaction is set off by the high-molecular-weight polyalkenoic acid. This acidic molecule exposes a micro-porous collagen network by selectively dissolving hydroxyapatite crystals. Additionally, ionic bonding takes place between the carboxyl groups of the



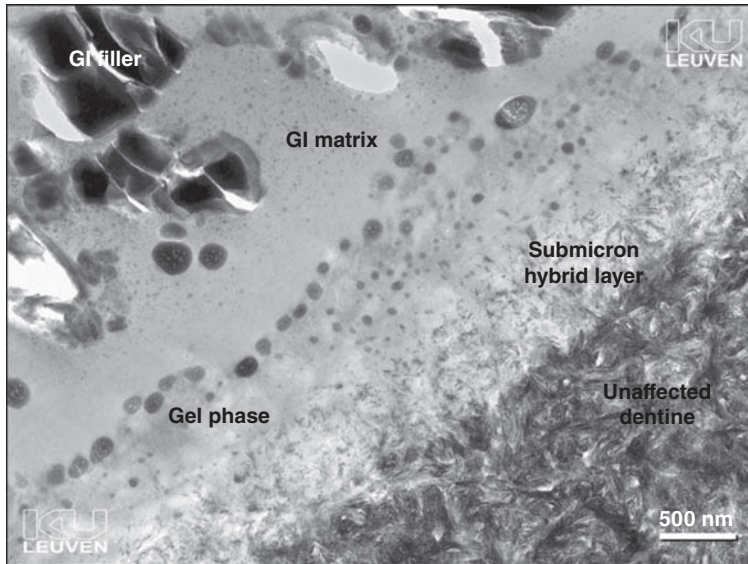
4.12 Combined TEM photomicrograph and schematic explaining the two-fold micro-mechanical (hybrid layer) and chemical interaction mechanism of glass ionomers. On top of the hybrid layer, a typical gel phase is deposited with some glass ionomers as a polycarboxylate salt with calcium that was released from the underlining dentine.

polyalkenoic acid and calcium of remaining hydroxyapatite crystals. This bond has been proven to be relatively stable, capable of withstanding ultrasonic rinsing.⁴¹

Micro-morphologically, a shallow hybrid layer of 0.5–1 μm is formed (Fig. 4.13). Because of a mild and partial demineralization, hydroxyapatite crystals can be distinguished around the collagen fibrils within the hybrid layer. Typically, a ‘gel phase’ closely attached to the hybrid layer can be observed with some glass ionomers. This amorphous phase on top of the interface has been reported to represent a salt of calcium polycarboxylate.^{55,56}

A conditioning step with a weak PAA significantly improves the bond strength.⁵⁷ Its beneficial effect on bond strength lies in a three-fold mechanism: (a) the removal of the smear layer by PAA; (b) a shallow demineralization of the tooth tissue; (c) a chemical interaction of PAA with residual hydroxyapatite.⁴¹

Clinically, the good adhesion of glass ionomers and resin-modified glass ionomers is striking. Very high retention rates of more than 90% have been observed for periods of up to five years in non-carious cervical lesions.^{26,58,59} Moreover, a recent study has revealed that glass-ionomer retention rates exceed by far the retention rates of other adhesives.²³ Other advantages of glass ionomers are their biocompatibility and their fluoride release. The main drawback of glass-ionomer restorations remains their inferior esthetic and mechanical properties as compared with composites.



4.13 TEM photomicrograph illustrating the interface of a resin-modified glass ionomer (FujiBond LC, GC) with dentine. Note the formation of a submicron hybrid layer, which results in an interfacial ultrastructure resembling that of a 'mild' self-etch adhesive. Within this hybrid layer, hydroxyapatite is available for additional chemical interaction with the polyalkenoic acid of the glass ionomer. On top of the hybrid layer, a typical gel phase representing a calcium polycarboxylate salt is deposited.

4.4 Current concerns of one-step adhesives

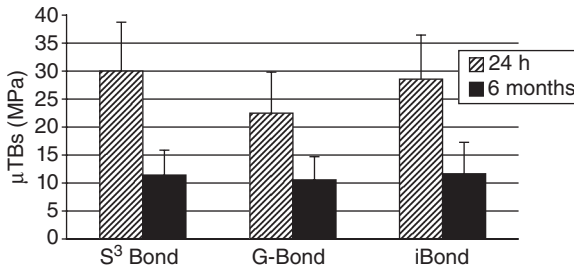
One-step self-etch adhesives (1-SEAs) are marketed as the most user-friendly adhesives. *In vitro* and *in vivo* research, however, revealed considerable shortcomings related to many of these simplified adhesives.

4.4.1 Reduced bond strength

The relatively low bond strengths obtained by 1-SEAs are a major concern (Fig. 4.5). Compared with multi-step self-etch and etch&rinse versions, one-step self-etch adhesives consistently achieve lower bond strengths.^{16,25,60,61} Clinically, these lower initial mechanical properties must particularly jeopardize their performance in minimally invasive cavities, and thus narrow and deep cavities. Many 1-SEAs might not be able to withstand the resultant high polymerization shrinkage stress, giving rise to early failures and postoperative sensitivity.⁶²

4.4.2 Reduced bond durability

Due to their high hydrophilicity, cured one-step self-etch adhesives have been demonstrated to act as permeable membranes, permitting water



4.14 Micro-tensile bond strength of three one-step adhesives to dentine after 24 h and 6 months of water storage.

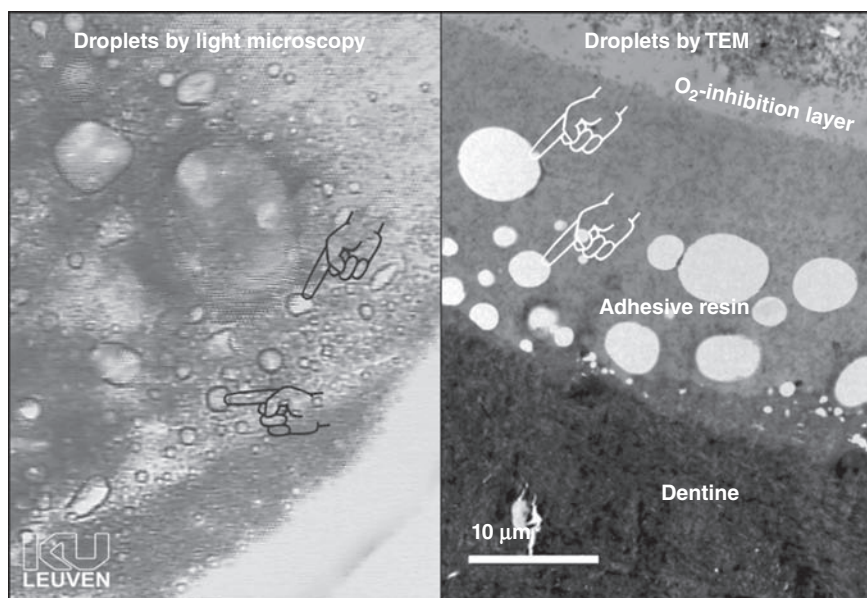
movement across the adhesive layer.^{63,64} Reticular patterns of nano-leakage, so-called ‘water trees’, have been found within the adhesive layer of 1-SEAs and are considered as sites of incomplete water removal and subsequent suboptimally polymerized resins.⁶⁵ The actual clinical relevance of these water trees remains unclear, but as they may function as water ducts, they may contribute to accelerated degradation of tooth–resin bonds.^{20,66,67} The micro-tensile bond strength of some recent-generation one-step adhesives was found to significantly reduce upon water storage of the micro-specimens in water for six months (Fig. 4.14).

4.4.3 Technique sensitivity

All 1-SEAs are very complex mixtures of monomers, solvents and filler particles. These blends of hydrophilic and hydrophobic components have to fulfill all adhesive tasks – namely etching, priming and bonding – in a single step.⁸ This renders them rather sensitive to application mistakes. In particular, the air-drying step subsequent to their application is crucial to reduce the amount of solvent and water in the adhesive layer as much as possible. It is known that thick adhesive layers of simplified adhesives decrease bond strengths tremendously.⁶⁸ On the other hand, this air-drying procedure should also be done in such a way that a sufficient amount of monomers is kept at the surface to provide sufficiently good mechanical properties to the adhesive layer. In narrow and complex cavities, the correct balance between too much and not enough air-drying is difficult to achieve; while the adhesive may still pool in the cavity corners, the amount of monomers on the cavity walls may already be too low.⁶⁹

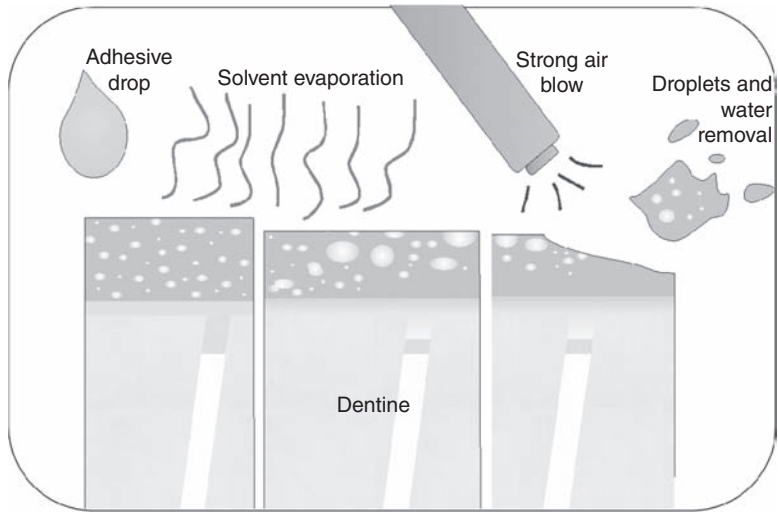
4.4.4 Hydroxy ethyl methacrylate (HEMA)-free formulation

More recently, complex processes of phase separation have been shown to occur in one-component, HEMA-free SEAs (Fig. 4.15).^{69,70} As soon as such



4.15 Light microscopy and TEM photomicrographs illustrating the formation of droplets due to phase separation within HEMA-free one-step adhesives. O₂-inhibition layer, oxygen inhibition layer.

an adhesive was dispensed onto a glass plate and the solvent started to evaporate, simple light microscopy of one-step adhesive solutions revealed a phase separation, yielding a multitude of droplets that slowly emerged towards the top of the adhesive drop and then disappeared. If the adhesive was light-cured, all remaining droplets were entrapped in the adhesive layer. The explanation for these observations must be found in the complex mixture of both hydrophobic and hydrophilic components, dissolved in an organic solvent (usually ethanol or acetone). Gradual evaporation of the solvents sets off the phase-separation reaction, in which water separates from the other adhesive ingredients. HEMA plays a key role in this process, as this monomer acts as a wetting agent due to its hydrophilic character and can prevent water from separating from other adhesive ingredients. It is self-evident that the incorporation of droplets may contribute to bond degradation, but persistence of water in the adhesive layer may also affect the bond strength adversely. However, somewhat surprisingly, no direct negative effect of the entrapped droplets on the ultimate or fatigue strength of adhesive bonds was noted.⁷¹ Moreover, these phase separations have been regarded as beneficial, as they offer a way to remove water from the adhesive interface (Fig. 4.16). Air-blowing of the primed surface will accelerate the evaporation of the solvent (acetone), by which water separates

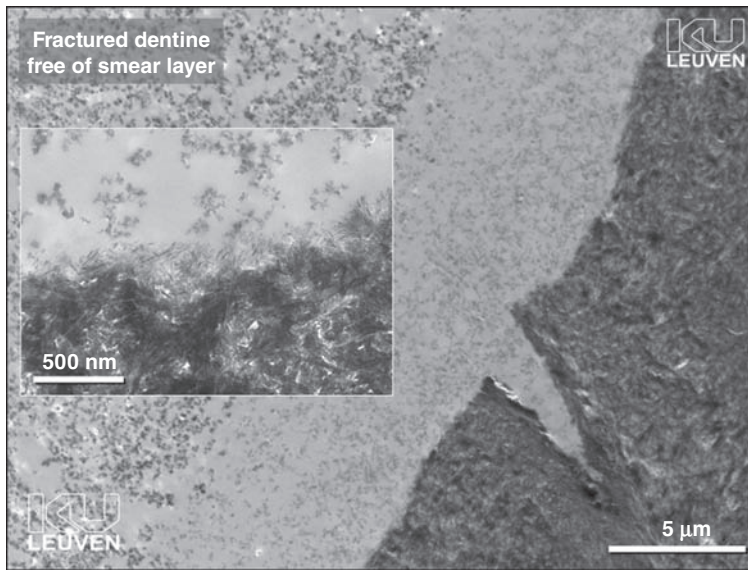


4.16 Schematic illustrating the concept of HEMA-free, one-step self-etch adhesives that make use of the solvent evaporation-initiated phase separation between water and the other adhesive ingredients to remove most of the water from the adhesive interface.

from the other adhesive components. The resultant droplets can then be removed from the adhesive by a prolonged thorough air-blowing (using maximum air pressure). In this way, HEMA-free, one-step self-etch adhesives possess a kind of built-in, relatively technique-insensitive, method of achieving a low-water-containing adhesive interface.

4.4.5 Hydroxy ethyl methacrylate (HEMA)-rich formulation

In order to avoid phase separation, HEMA can be added to the adhesive formulation, as explained in Section 4.4.4. One study has demonstrated that a relatively high HEMA concentration is required to avoid phase separation.⁶⁹ Such HEMA-rich adhesives are, however, prone to other problems, in particular a higher sensitivity to water absorption from the outside environment as well as from the host dentine. When HEMA is cured in the presence of water, polymerization is incomplete and a porous hydrogel is formed. These areas of increased permeability allow water to permeate through the adhesive layer, compromising in particular the long-term bonding effectiveness.⁴² Another, but related phenomenon is osmosis. The HEMA hydrogel produced upon curing of the all-in-one adhesive can act as a semi-permeable membrane,⁶⁴ of which the upper layer that is insufficiently polymerized due to oxygen inhibition is a hypertonic fluid. Both effects combined result in an osmotic transfer of water from the underlying dentine towards the adhesive-composite interface. As this is a time-

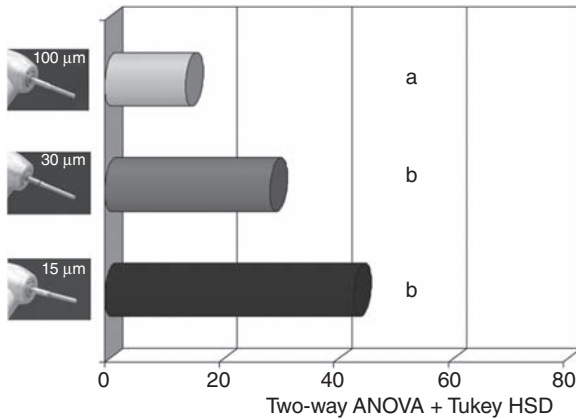


4.17 TEM photomicrographs showing the adhesive–dentine interface produced by the ‘ultra-mild’ (pH = 2.7), one-step self-etch adhesive (Clearfil S³ Bond, Kuraray) when applied to fractured dentine. Only a very shallow hybrid layer of a few hundreds of nanometers was formed.

dependent process, postponing the curing of the overlying composite will result in severe droplet formation and premature failure at the adhesive–composite interface.⁴² Although, in principle, this is valid for all one-step self-etch adhesives, HEMA-rich adhesives are much more sensitive to this osmotic breakdown.⁷⁰ Due to the higher amount of small (HEMA) molecules, the interface produced by an HEMA-rich adhesive is more permeable; this fact, in combination with the high osmotic pressure at the oxygen-inhibition layer, may explain why this osmotic blistering is a major problem for HEMA-rich adhesives and almost no problem for HEMA-free adhesives.⁷⁰

4.4.6 ‘Ultra-mild’ self-etch adhesive

In particular, the low stability of functional monomers in low pH solutions^{72,73} has driven some manufacturers to produce ‘ultra-mild’ self-etch adhesives, such as Clearfil S³ Bond (Kuraray). TEM revealed that such an adhesive with a relatively high pH (≈ 2.7) decalcified the dentine surface only very superficially for up to a few hundreds of nanometers, with few collagen fibrils exposed at the interface (Fig. 4.17). This particular interfacial feature has therefore been termed a nano-interaction zone.⁷⁴ The key factor in this ultra-mild approach is the unique property of the functional monomer 10-MDP that has currently been documented with the significantly highest



4.18 Micro-tensile bond strength of the ‘ultra-mild’, one-step self-etch adhesive (Clearfil S³ Bond, Kuraray) to dentine when prepared by diamond burs with different grit sizes. Different letters represent statistical significance (two-way ANOVA and Tukey HSD: $p < 0.05$).

chemical bonding potential (Fig. 4.10).⁴ However, this nano-interaction approach also re-introduced the above mentioned smear-layer ‘obstacle’. ‘Mild’ self-etch adhesives ($\text{pH} \approx 2$) dealt relatively effectively with the smear layer, even when produced by various surface preparation methods such as diamond burs with different grit sizes, air-abrasion and sono-abrasion.^{32,75} Due to their increased pH, the newly introduced ‘ultra-mild’ self-etch adhesives are much more sensitive to the smear-layer characteristics. For example, Clearfil S³ Bond performed significantly better when an extra-fine (15μm grit-size) diamond bur was used, as opposed to a more commonly used regular (100μm grit-size) bur (Fig. 4.18) (R. B. Ermis *et al.*, unpublished observations, 2007). If this is clinically relevant, it should definitely be investigated.

4.4.7 Reduced shelf-life

Most resins used in dental adhesives are acrylates or methacrylates. The ester groups of these resins are prone to hydrolysis, especially in an acidic environment.^{72,73,76} This degradation results in the formation of acids such as methacrylic acid; this enhances the self-etching aggressiveness but is not necessarily accompanied by the needed deeper resin infiltration.⁷² Most of the currently commercially available adhesives are prone in some way to such an in-the-bottle monomer degradation.⁷³ One way to overcome this problem is by producing water-free adhesives (e.g. Absolute 2, Dentsply-Sankin), since the monomer degradation is a hydrolytic process

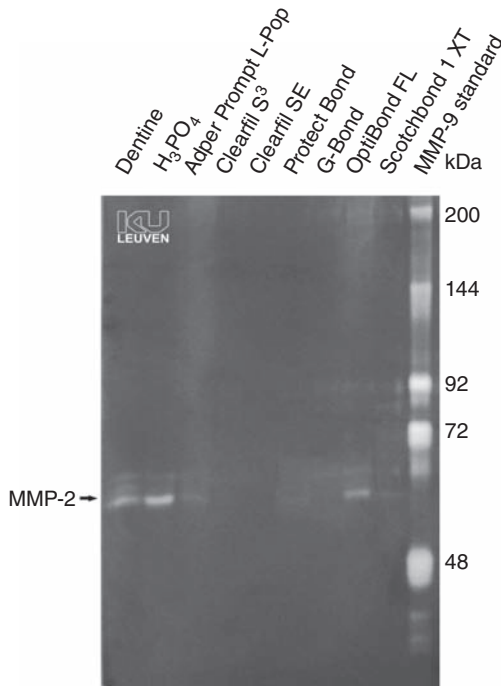
that will not take place in a water-free environment. In order to activate etching, such a water-free adhesive should be applied to a wet surface, which immediately creates the problem of how wet the surface should be. Two-component one-step adhesives keep water separate from the functional monomers (e.g. Adper Prompt L-Pop, 3M ESPE; Futurabond NR, VOCO; One-up Bond F Plus, Tokuyama; Reactmer Bond, Shofu; Tyrian SPE, Bisco; Xeno III, Dentsply). More recently synthesized monomers such as amide-linked polymerizable analogs, instead of conventional ester derivatives, and phosphonic-acid monomers instead of phosphoric-acid monomers (both in AdheSE, Ivoclar-Vivadent) are more hydrolytically stable,⁷³ which should improve the shelf-life of the adhesives.

4.4.8 Enzymes

Currently, bonding to dentine is achieved primarily through hybrid-layer formation, either relatively deep with etch&rinse adhesives and low-pH 'strong' self-etch adhesives, or relatively superficial with 'mild' and 'ultra-mild' self-etch adhesives. The resultant hybrid layer then, respectively, consists of a completely or partially hydroxyapatite-deprived collagen mesh infiltrated by resin. It has been shown that dental adhesives during the production of this hybrid layer can also release enzymes from the dentine matrix that have a low collagenolytic activity.⁷⁷ Such host-derived enzymes can hydrolyze the collagen fibrils that make up the hybrid layer and so compromise the long-term clinical bonding effectiveness. Recent enzymographic research revealed that collagenase A is mostly responsible for the hydrolytic breakdown of the hybrid layer (Fig. 4.19).^{78,79} The actual relevance of this enzymatic breakdown of the hybrid layer may, however, be less dramatic clinically than has been suggested in some papers, as the endogenous enzymes gradually decrease with age, generally disappearing before the age of 40.⁸⁰ A method of protecting the interface against such enzymatic degradation processes is the use of matrix metalloproteinases inhibitors, of which one, chlorhexidine, is already commonly used in dentistry and seems effective *in vitro* as well as *in vivo*.^{81,82}

4.5 Clinical performance of current adhesives

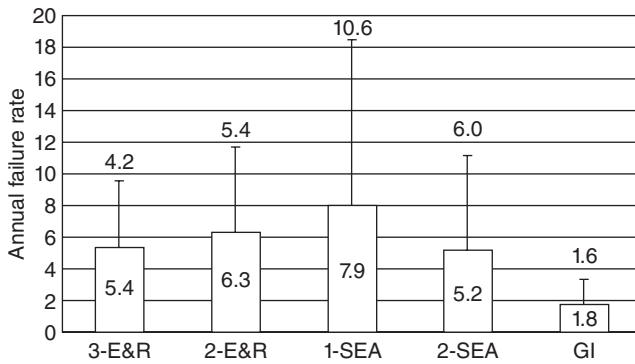
The ultimate method of testing dental adhesives is performing clinical trials. If the study objective is to investigate the bonding effectiveness of adhesives, only studies involving non-carious class-V adhesive restorations should be considered; there are many reasons for this.¹¹ The main reason is that only class-V lesions do not provide any macro-mechanical retention, so that ineffective bonding will result in early restoration loss, which is the only objective parameter available. In a recent systematic review,²³ the



4.19 SDS-PAGE test of different adhesive primers mixed with dentin powder for 30s. Matrix metalloprotease-2 (MMP-2) (gelatinase-A) was released by etching with phosphoric acid and the etch&rinse adhesives, and also slightly by the 'strong', one-step self-etch adhesive (Adper Prompt L-Pop, 3M ESPE).

retention rate of different commercial adhesives that were tested in clinical class-V studies worldwide was registered per category of adhesive approach in order to get a better idea of the clinical effectiveness of today's adhesives. In this study, the following main conclusions were drawn (Fig. 4.20):

- Regarding retention rate of class-V restorations, glass ionomers bonded most effectively and durably to tooth tissue.
- Among the resin-based adhesives, the three-step etch&rinse adhesives and the 'mild', two-step self-etch adhesives showed a clinically reliable and predictably good clinical performance with retention rates generally well above the American Dental Association (ADA) specifications.
- The clinical effectiveness of two-step etch&rinse adhesives was less favorable than that of their three-step etch&rinse precursors.
- A strongly varying and often inefficient clinical performance was noted for the one-step self-etch adhesives.



4.20 Annual failure rates of adhesive class-V restorations per adhesive category. GI, glass ionomer.

Thus, although the one-step adhesives with the most simplified application procedure are clinically faster and easier to use, they generally perform less well. The strongly varying results measured at different research centers point to a relatively high technique sensitivity, in contrast with what is often claimed by manufacturers. It definitely should be mentioned that the most recent generation of one-step self-etch adhesives appear to perform better clinically, as is suggested by a more recent review of class-V clinical data (A. Mine *et al.*, unpublished data, Catholic University of Leuven, 2007).^{83–86} These promising short-term (1–2 year) results are however, still far from the near to perfect long-term (7–13 year) results of a gold standard, three-step etch&rinse adhesive.^{87,88}

4.6 Conclusion

A good classification of adhesives is indispensable for maintaining an overview of the current field. The strength of the proposed classification lies in its simplicity and its scientific basis. Each category in this classification is characterized by a specific bonding mechanism, a specific and distinct application protocol and by a specific interfacial ultrastructure as best imaged using TEM.

With regard to the actual bonding effectiveness, it is now very clear that an adhesive's *in vitro* and *in vivo* performance greatly depends on its specific ingredient composition and this is especially so for the more recent one-step self-etch adhesives. In spite of the improved ease-of-use and faster application, a simplified application procedure so far seems to entail a reduced bonding effectiveness, and the advantages of these adhesives should therefore be traded off against their major shortcomings. Presently, the most acceptable trade-off seems to be a 'mild', two-step self-etch

adhesive that combines micro-mechanical interlocking to the tooth substrate with additional chemical interaction which definitely contributes to the bond stability.

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Mechanical stability of resin–dentine bonds

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5.1 Introduction

5.1.1 Mechanical consequences of etching dentine

Resin–dentine bonds are created by acid-etching dentine to remove smear layers and demineralize dentine enough to increase its surface porosity and create resin tags. Solvated comonomers are then applied to replace the volume of extracted mineral with polymerized resin. The original composition of dentine has been reported to be 45 vol% mineral, 48 vol% collagen and 7 vol% water (Kinney *et al.*, 1994). The stiffness of mineralized dentine is 17–20 GPa and its tensile strength is about 100 MPa. After dissolving the mineral phase with acid conditioner and rinsing with water, the demineralized dentine is 48 vol% collagen and $45 + 7 = 52$ vol% water. During infiltration of the demineralized dentine by solvated comonomers, water is supposed to be completely displaced and replaced. When the solvent is evaporated, the matrix shrinks in proportion to the solvent concentration, while the comonomer concentration rises. This results in matrix shrinkage down to the pure comonomer volume.

Recent work has demonstrated that the thickness of the hybrid layer depends upon how deeply the matrix is etched by the acid, how much solvated comonomers infiltrate into the demineralized matrix and how much the matrix shrinks when the solvents are evaporated. Presumably, the strength of the hybrid layer would be proportional to the strength of the collagen fibrils, times their volume fraction, plus the volume fraction of the resin times its strength which depends upon how well it is polymerized and how well it is cross-linked by dimethacrylates. The stiffness of hybrid layers would depend upon the modulus of elasticity of the resin infiltrated into the matrix (c. 3–4 GPa) times its volume fraction and the modulus of elasticity of the collagen fibril matrix times its volume fraction.

Before resin infiltration, the modulus of elasticity of demineralized dentine matrix saturated with water has been reported to be as low as 100 kPa (Balooch *et al.*, 1998) measured in compression, or 1–5 MPa in tension

(Maciel *et al.*, 1996). While the modulus of elasticity of collagen molecules is 1–2 GPa (Sasaki and Odajima, 1996; Katz *et al.*, 2003), the modulus of elasticity of collagenous fibrous matrices or scaffolds is only about 1 MPa because the volume fraction of collagen is 0.3 while the volume fraction of the water-filled pores is 0.7 (D. Pashley, unpublished observation, 2006). Under compressive stress, the water is extruded from the matrix and the collagen fibrils come closer together until there is no space between the fibrils. Under this condition, the compressed, collapsed collagen matrix would have a modulus of elasticity of 1–2 GPa, which reflects the actual stiffness of collagen molecules. However, in collagenous matrices infiltrated with adhesive resin, the stiffness of the hybrid layer should be between that of collagen (1–2 GPa) and that of the resin (3–4 GPa).

5.1.2 Mechanical consequences of resin infiltration

In simple experiments where resins were infiltrated into demineralized, dehydrated dentine for hours to create ‘perfect’ hybrid layers, Sano *et al.* (1995c) reported that these ‘hybrid layers’ had a modulus of elasticity of 3.6 ± 0.8 GPa and a toughness of 27.7 MN/mm^3 . Although the modulus of elasticity is low, the toughness of resin-infiltrated dentine was higher than that of mineralized dentine. In that same paper, Sano *et al.* (1995c) measured the tensile strength of adhesive resins; they varied from 31–83 MPa with moduli of elasticity between 0.8 and 2.1 GPa. Thus, while the ultimate tensile strength of acid-etched dentine can be restored to that of normal mineralized dentine (c. 100 MPa), the modulus cannot be restored because the moduli of resins are 3–4 GPa, while that of hydroxyapatite is 100 GPa. Using more sophisticated techniques, Van Meerbeek *et al.* (1993) reported that the modulus of elasticity of resin-bonded dentine was 4.9–9.7 GPa by nanoindentation. Using atomic force microscopy (AFM) Schulze *et al.* (2005) reported that hybrid layers created by Clearfil SE Bond had indentation moduli of 5–6 GPa while those made by Single Bond were less than half as stiff. This more recent work showed that in the presence of water, the mechanical properties of both resins and dentine matrices fall significantly.

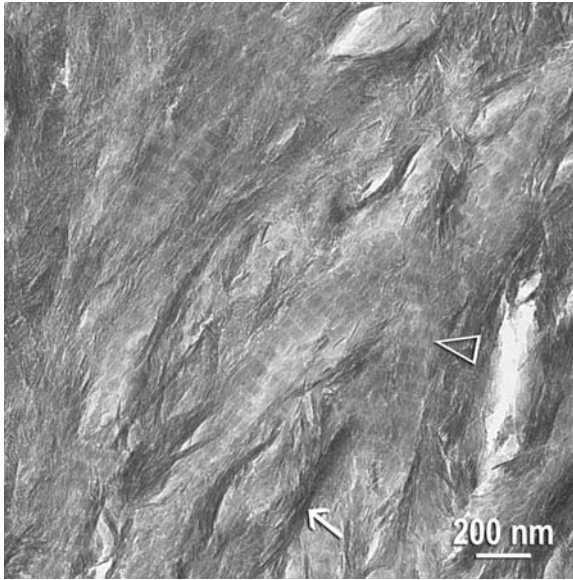
The generation of hybrid layers creates a three-dimensional ‘interphase’ of a new hybrid material. This is a very strong collagen fibril-reinforced resin composite (tensile strength of c. >100 MPa). When resin–dentine bonds are stressed in tension to failure, if the stressing is done uniformly, the failures usually occur between the top of the hybrid layer and the bottom of the adhesive layer. These failures are generally ‘interfacial’, not ‘interphasial’. The presence of air bubbles, water droplets, resin globules, poor wetting, etc. create regions of high stress concentration at the interface of the resin and hybrid layer. The fact that one sees cohesive failures in the hybrid layer

probably indicates non-uniform stressing. Because hybrid layers are only 1–5 µm thick, they are very difficult to study. It is likely that dimethacrylates in water/alcohol-based adhesives such as Scotchbond Multi-Purpose or Single Bond, do not penetrate hybrid layers uniformly. That is, they may only infiltrate the top-third of the hybrid layer, allowing monomethacrylates such as hydroxy ethyl methacrylate (HEMA) to penetrate more deeply. When polymerized, the top halves of such hybrid layers would have more cross-links and be stiffer than the bottom halves. When stressed, the top and bottom of the hybrid layers would undergo different degrees of strain and hence, of stress, inducing failures within their ‘phases’.

When manufacturers mixed relatively hydrophobic dimethacrylates {2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)]-phenyl propane (BisGMA); triethyleneglycol dimethacrylate (TEGDMA); urethane dimethacrylate (UDMA)} with more hydrophilic monomers in a single bottle, their resin coatings behaved as if they contained continuous hydrophilic channels that spanned the full thickness, but were surrounded by hydrophobic domains. It is felt that this is responsible for the water permeability of polymerized ‘simplified’ adhesives. We speculate that the mechanical stability of resin–dentine bonds depends upon the stability of the adhesive resin component of the hybrid layer and the stability of the collagenous matrix of the hybrid layer.

5.1.3 Goals of resin infiltration of demineralized dentine

Before discussing the mechanical stability of resin–dentine bonds, it is appropriate to examine how well these bonds are created initially. Dentine is a natural, biological composite that consists of the impregnation of plate-like apatite crystallites of nanometer dimensions within the intrafibrillar and interfibrillar spaces of a collagen network (Fig. 5.1). It is known that both the intrafibrillar and interfibrillar apatites are responsible for the mechanical properties of dentine (Kinney *et al.*, 2003). Intrafibrillar crystallites, in particular, are deposited in an orderly manner within the gap zones that exist among adjacent tropocollagen entities (Traub *et al.*, 1989; Jäger and Fratzl, 2000). In the absence of intrafibrillar mineralization, such as in dentine derived from individuals with dentinogenesis imperfecta, the hardness and modulus of elasticity (stiffness) of such altered dentine has been shown to be inferior to those of sound, mineralized dentine (Kinney *et al.*, 2003). It is prudent to point out that sound, mineralized dentine, in the absence of partial demineralization, exists as a relatively stable composite. Small sticks of mineralized dentine showed no changes in mechanical properties over one year of incubation (Carrilho *et al.*, 2005a). The intrafibrillar and interfibrillar mineral crystallites protect the soft collagen fibril from denaturation induced by external challenges such as heat (Bigi *et al.*, 1991),



5.1 Mineralized dentine is a biological composite of a collagen fibril matrix filled with nanometer-sized apatite crystallites located both within (intrafibrillar; open arrowhead) and between (interfibrillar; arrow) collagen fibrils.

exogenous bacterial collagenases (Wang *et al.*, 2002) and sodium hypochlorite (De Munck *et al.*, 2007).

The reliance on hybridization of partially demineralized hard tissues by adhesive resin monomers as a bonding mechanism to dentine has not changed since Nakabayashi *et al.* (1982) introduced this exciting concept a quarter of a century ago. Theoretically, resin hybridization of dentine should achieve three functions: (1) provide micromechanical and/or chemical retention of methacrylate resin-based restorations; (2) restore the mechanical properties of the partially demineralized dentine to approximate those of the original undemineralized dentine; (3) protect the collagen fibrils within the hybridized dentine against subsequent exogenous and endogenous denaturation challenges, in a manner that is analogous to the protective function of the apatite phases in mineralized dentine. Ideally, dentine hybridization should completely replace the bulk water that occupies the interfibrillar and intrafibrillar spaces of demineralized collagen fibrils by resin monomers that polymerize *in situ*. This ensures the absence of interfaces between the collagen fibrils and resins, making the hybridized dentine resistant to subsequent degradation. If only interfibrillar hybridization is achieved, an interface will be present between the interfibrillar resin and

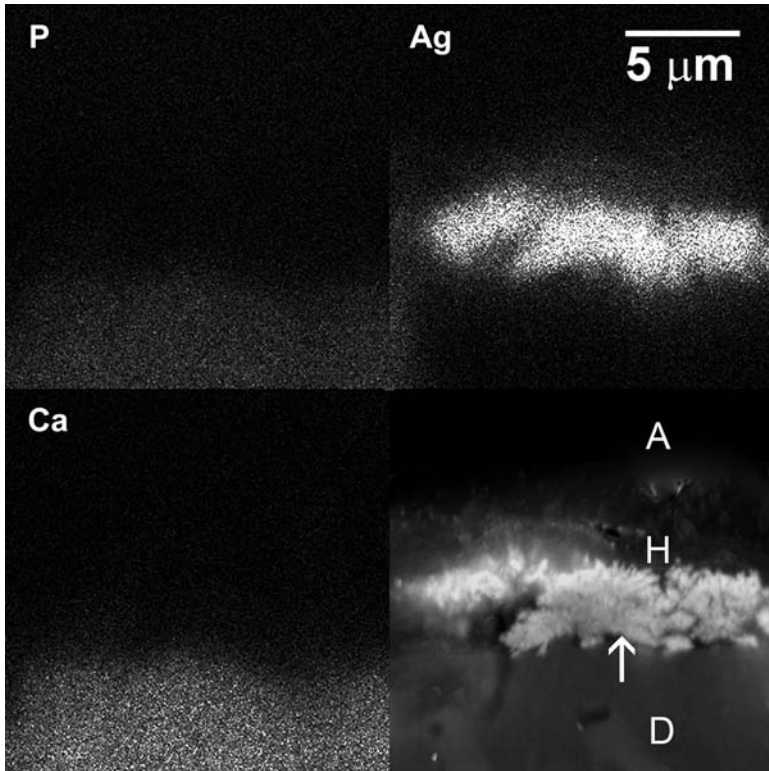
the collagen fibril (Tay *et al.*, 2000), allowing the resin to be pulled out from the surrounding resin during rupture, instead of fracturing with the resin (Nakabayashi and Pashley, 1998). From a more realistic perspective, perfect interfibrillar resin infiltration has seldom been encountered with the use of contemporary etch-and-rinse and self-etch adhesives. This may be due to the presence of a resin diffusion gradient between the top and bottom of a thick demineralized collagen matrix (Van Meerbeek *et al.*, 1992). These sites of incomplete interfibrillar resin infiltration occur within gap-free dentine hybrid layers. The presence of porosities within resin-bonded interfaces is called nanoleakage.

5.1.4 Nanoleakage – measuring porosity of bonded interfaces

Nanoleakage (Sano *et al.*, 1995a, 1995b) distinguishes nanometer-sized porosities within hybrid layers from visibly discernible, 10–20 µm wide gaps between restorative materials and cavity walls; the latter is classified as microleakage.

Nanoleakage can be detected in hybrid layers created in both etch-and-rinse and self-etching adhesives when these interfaces were immersed in a silver nitrate tracer solution (Sano *et al.*, 1995a, 1995b). The silver nitrate is reduced into silver granules that are deposited as reticular patterns within the interfibrillar spaces of the hybrid layer, which are then observed using the back-scattered mode of a scanning electron microscope (Fig. 5.2) or in thin sections prepared for transmission electron microscopy (TEM) (Fig. 5.3). Nanoleakage has also been observed using confocal light microscopy when a fluorescent dye such as rhodamine (Fig. 5.4) was used as a tracer (Pioch *et al.*, 2001). The clinical significance of nanoleakage was initially that it identified uninfiltreated interfibrillar spaces. These spaces were too small to permit bacterial penetration, but were large enough for enzymes to enter. It was hypothesized that nanoleakage revealed the location of defects at the resin–dentine interface, and could be the pathway for degradation of resin–dentine bonds over time.

When a 50% ammoniacal silver nitrate tracer solution was employed instead of regular aqueous solutions, two different modes of nanoleakage expression were also seen. The first mode consisted of the reticular interfibrillar deposits within the hybrid layer that were originally depicted using the conventional acidic (pH 4.5) silver nitrate solution. The second mode consisted of spotted silver grains that were seen within the adhesive layer and the hybrid layer (Tay *et al.*, 2002). These isolated spotted silver grains were thought to represent interaction of the cationic diamine silver ion complexes with the anionic functional groups of the hydrophilic resin



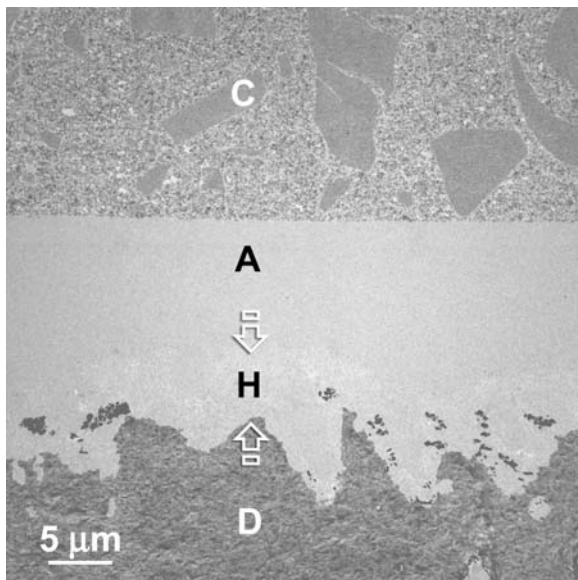
5.2 Reticular patterns of silver nanoleakage (arrow) within interfibrillar spaces of the hybrid layer (H) seen in back-scattered scanning electron microscopy (SEM). A, adhesive; D, dentine. The hybrid layer is devoid of calcium (Ca) and phosphorus (P), but contains silver (Ag) deposits.

monomers present in the polymer matrices of these adhesives (Fig. 5.5). The locations depicted by these spotted silver grains probably represent sites where subsequent water sorption within the polymer matrix occurs via hydrogen bonding (Zaikov *et al.*, 1988). For example, the spotted mode of nanoleakage expression in the hybrid layer and the adhesive layer was found to increase after water sorption. Nanoleakage patterns can change over time (Li *et al.*, 2001; Tay *et al.*, 2003a; Reis *et al.*, 2007).

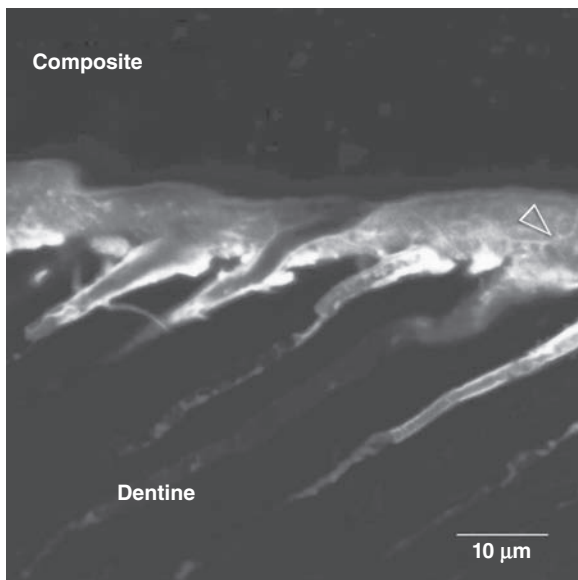
5.2 Permeability of adhesive resins to water

5.2.1 Water sorption of adhesive resins

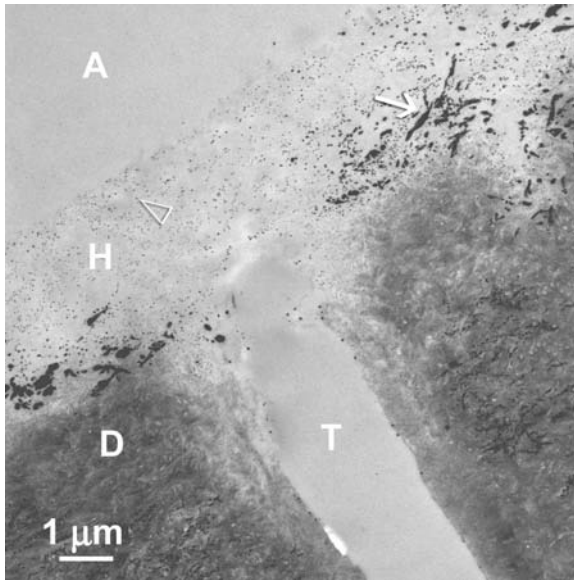
Very few polymers are absolutely impermeable to water. Water transport in polymer systems is related to the availability of molecular-sized pores in



5.3 Nanoleakage patterns in hybrid layers (H; between open arrows) shown by transmission electron microscopy. (C, composite; A, adhesive; D, dentine.)



5.4 Nanoleakage (open arrowhead) revealed using the fluorescent dye, rhodamine, and imaged in a confocal laser scanning microscope.



5.5 Spotted silver grains (open arrowhead) from ammoniacal silver nitrate nanoleakage within a hybrid layer (H) created by infiltration of hydrophilic dental polymers into acid-etched dentine. Arrow, reticular pattern of nanoleakage along interfibrillar spaces: A, adhesive; D, dentine; T, dentinal tubule.

the polymer structure and the affinity of the polymer components with water (Marom, 1985; Zaikov *et al.*, 1988; VanLandingham *et al.*, 1999). The availability of nanopores depends on the polymer microstructure, morphology and cross-link density, which are functions of degree of cure, stoichiometry, molecular chain stiffness and the cohesive energy density of the polymer (Soles *et al.*, 2000). The affinity of the polymer to water is related to the presence of hydrogen bonding sites along the polymer chains which create attractive forces between the polymer and water molecules (Soles and Yee, 2000). The water molecules that are free to move through the holes, or the free volume of the polymer, are often referred to as ‘unbound’ molecules. By contrast, water molecules that attach to the polymer chain via hydrogen bonding, referred to as ‘bound’ molecules, disrupt interchain hydrogen bonding, inducing swelling, plasticizing of the polymer, reducing its glass transition temperature and decreasing the mechanical properties and stability of the polymerized resins (Nogueira *et al.*, 2001; Ito *et al.*, 2005a, 2005b).

Water and ions can move across a polymer matrix by hopping from one hydrophilic domain to another (Dürr *et al.*, 2002). This ion hopping

mechanism has been commonly observed in polymeric ionic conductors, in which ionic salts are incorporated in a polar polymer that possesses significant ionic conductivity (Frisch and Stern, 1983). Diffusion of water molecules through a polymer matrix occurs via micro-cavities of different sizes that are formed and destroyed almost instantaneously in the polymer (Müller-Plathesup *et al.*, 1993). The more hydrophilic the polymer, the greater is the ease of formation of these micro-cavities, because of the reduced energy required to disrupt the adjacent polymer chains (Soles and Yee, 2000). In the context of dentine adhesives, these hydrophilic domains may be visualized as fine, discrete silver grains (i.e. the spotted mode of nanoleakage) in the adhesive after immersion in ammoniacal silver nitrate (Tay *et al.*, 2002).

Although methacrylate-based resin monomers such as BisGMA, TEGDMA, UDMA or bisphenol A dimethacrylate exhibit water sorption and solubility to variable extents (Sideridou *et al.*, 2003; Ito *et al.*, 2005b), their permeability to water increases when hydrophilic resin monomers such as HEMA and 4-methacryloyloxyethyltrimellitic acid (4-MET) are mixed into the blend (Patel *et al.*, 2001; Unemori *et al.*, 2003). Contemporary dentine adhesives are rendered very hydrophilic in order to improve their bonding to intrinsically wet substrates such as dentine (Malacarne *et al.*, 2006). The incorporation of high concentrations of hydrophilic and/or ionic methacrylate-based resin monomers increases their attraction of water, leading to increased water sorption (Yiu *et al.*, 2006b; Nishitani *et al.*, 2007). In conventional three-step etch-and-rinse adhesives and two-step self-etching adhesives, these hydrophilic and ionic resin monomers are employed sparingly in the form of primers. The primed dentine is eventually covered with a layer of comparatively hydrophobic bonding resin. This reduces the susceptibility of the bonded interfaces to water sorption as well as minimizes water being incorporated within the adhesive interface when the adhesive is applied to a wet dentine substrate, which in turn, improves the mechanical stability of resin–dentine bonds.

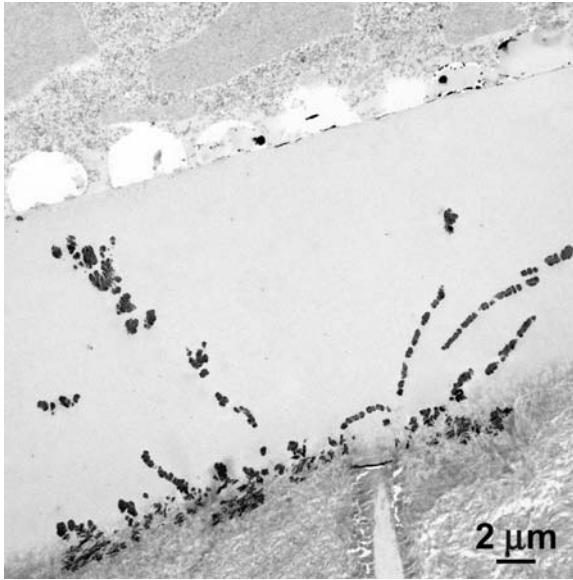
5.2.2 Consequences of water sorption by adhesive resins

Bond degradation is preceded by water sorption into a polymer matrix. Water sorption is enhanced by the presence of hydrophilic and ionic resin monomers (Tanaka *et al.*, 1999), which in turn facilitate ion movement within a polymerized resin matrix. The supramolecular structure of glassy polymers is normally not in equilibrium. A non-equilibrium structural state may be preserved for an unlimited period of time if the segmental mobility of macromolecules is ‘frozen’, as exemplified by storing a piece

of polymerized adhesive in a dry state below its glass transition temperature. Such a state is altered on water sorption, as the sorbed water acts as a plasticizer, that reduces the glass transition temperature of the polymer, increases the segmental mobility of the polymer chains and ‘defreezes’ the physical process of structural relaxation (Zaikov *et al.*, 1988). Although absorbed fluids may plasticize and induce relaxation in the adhesive polymer and swell the adhesive, leading to a loss of mechanical properties, degradation of the interface is the primary reason for failure of many adhesive joints (Kinloch, 1979). When multi-step etch-and-rinse and two-step self-etch adhesives were challenged with thermomechanical loading between 5 and 55°C and up to 100 000 cycles, their microtensile bond strengths fell 25–30%. Conversely, the microtensile bond strengths of single-step self-etch adhesives fell 50–80% after thermomechanical loading (Frankenberger *et al.*, 2005). When dentine bonded with the four different classes of adhesives (i.e. three-step etch-and-rinse, two-step etch-and-rinse, two-step self-etch and single-step self-etch adhesives) was directly exposed to water using miniature specimens that expedite water sorption, the microtensile bond strengths of the three-step etch-and-rinse adhesive and the two-step self-etch adhesive did not significantly decrease after one year of direct water storage. In contrast, the bonding effectiveness values of the two-step etch-and-rinse adhesive and one-step self-etch adhesives were reduced to almost zero after the same period of direct water exposure (De Munck *et al.*, 2006).

5.2.3 Morphological consequences of the presence of water trees

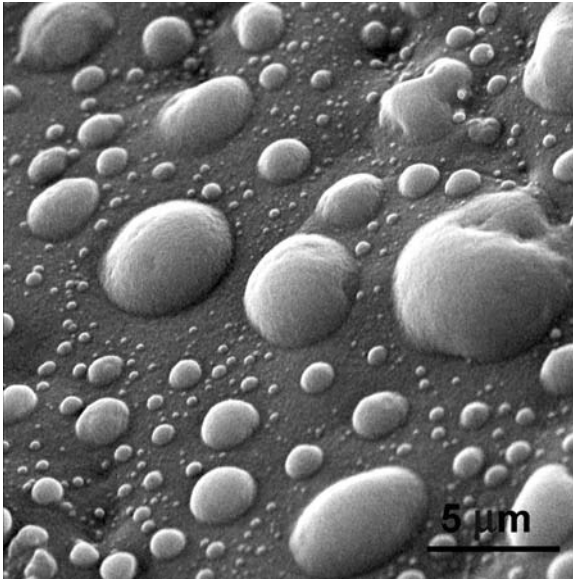
As marketed simplified etch-and-rinse and self-etch adhesives lack non-solvented resin coatings (Brackett *et al.*, 2005; Van Landuyt *et al.*, 2006), they behave as permeable membranes (Tay *et al.*, 2004c, 2004d) that permit rapid through-and-through water movement (Fig. 5.6) across the polymerized adhesives (Chieffi *et al.*, 2007) when they are applied on wet dentine even in the absence of simulated pulpal pressure. Dentinal fluid transudation across simplified dentine adhesives has been shown to occur when they were bonded to non-carious, deep, vital human dentine (Chersoni *et al.*, 2004; Tay *et al.*, 2004a), and even from dowel spaces created *in vivo* in endodontically treated teeth, which, presumably, contain water within the dentinal tubules (Chersoni *et al.*, 2005). These fluid droplets could be seen when impressions of the adhesive-coated dentine were taken using a relatively hydrophobic polyvinylsiloxane material and subsequently replicated with epoxy resin (Fig. 5.7). This phenomenon could be duplicated *in vitro* using bonded, extracted human teeth (Elgelaid *et al.*, 2004; Sauro *et al.*, 2006, 2007). Entrapment of water droplets that



5.6 Through-and-through water movement within polymerized adhesive layers in resin–dentine interfaces created by a very hydrophilic one-step self-etch adhesive. Water droplets that traversed the adhesive layer are trapped by the hydrophobic composite above and appear as hemispherical voids along the composite–adhesive interface.

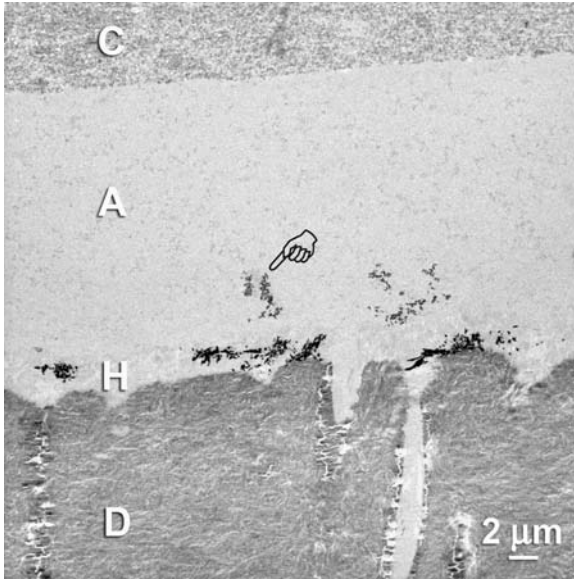
emerged from the adhesive surfaces during the slow polymerizing of chemical-cured resin composites (Carvalho *et al.*, 2004) also accounts for the apparent incompatibility when these composites were coupled to acidic adhesives in the presence of non-amine-type ternary catalysts (Cheong *et al.*, 2003; Suh *et al.*, 2003).

The fact that fluid transudation rapidly occurs across polymerized dentine adhesives implies that there are interconnected porosities or channels within the adhesives. This rapid water movement differs from the relatively slower diffusional processes across bulk resin. Unfortunately, these very minute channels cannot be seen with standard electron microscopic techniques, as the water is lost after desiccation of the specimens and the channels collapsed when specimens are examined under vacuum. The water channels that are present when simplified dentine adhesives are bonded to dentine may be ultrastructurally visualized by using ammoniacal silver nitrate as a tracer before processing of the bonded specimens for TEM. Different forms of silver-filled, interconnecting channels have been reported within the adhesive layers of some commercial brands of two-step etch-and-rinse and one-step self-etch adhesives

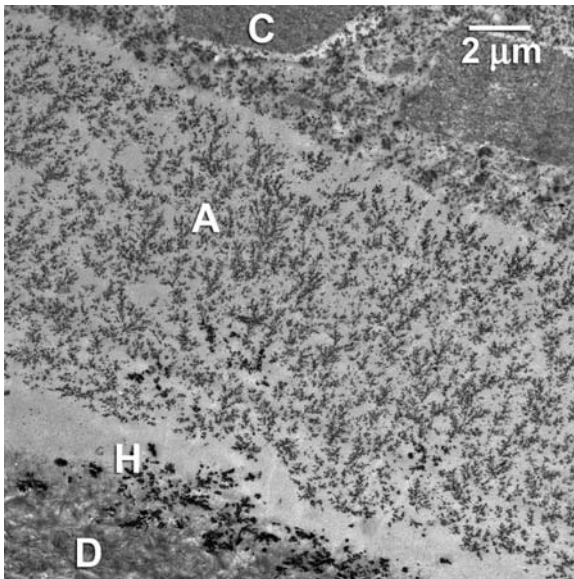


5.7 Scanning electron micrograph of epoxy resin replica of water droplets on the surface of a simplified one-step self-etch adhesive bonded to vital human dentine.

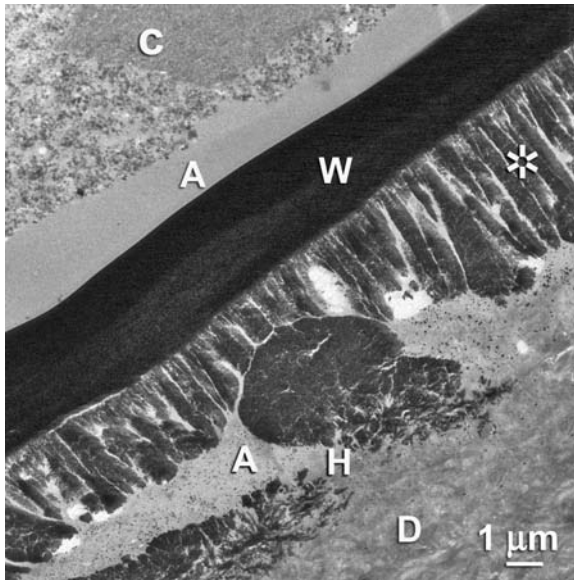
(Tay and Pashley, 2003b). The term ‘water trees’ was used to describe these silver-filled water channels within the adhesive layers. Water trees were predominantly located along, and perpendicular to, the surface of the hybrid layer, extending into the overlying adhesive layers. In their mildest forms, they appeared as isolated fractal-like, branched structures that extended from the surface of the bonded dentine into the adhesive layer (Fig. 5.8). In their most severe forms that are usually found in one-step self-etch adhesives, more than 50% of the adhesive layer could be occupied by heavy silver deposits, particularly after these interfaces were subjected to mechanical stress and water sorption (Fig. 5.9). Other water channels were seen ‘reflecting’ downwards from the junction between the adhesive and the resin composite (Fig. 5.10). These ‘reverse water trees’ (Tay *et al.*, 2005a) were thought to be caused by the redirection of water that reached the top of a partially polymerized adhesive layer from the heat generated during light-curing of a simplified adhesive. Occasionally, through-and-through channels that were oriented perpendicular to the hybrid layers could also be observed spanning the entire thickness of the adhesive layer (Tay and Pashley, 2003a; Ito *et al.*, 2005a). These through-and-through channels were often connected to hemispherical water droplets that were trapped between the adhesive and the resin composite



5.8 A mild form of silver-filled water trees (pointer) in the adhesive layer emanating from the hybrid layer (H) approximately perpendicular to the dentine surface (D). (C, composite; A, adhesive.)



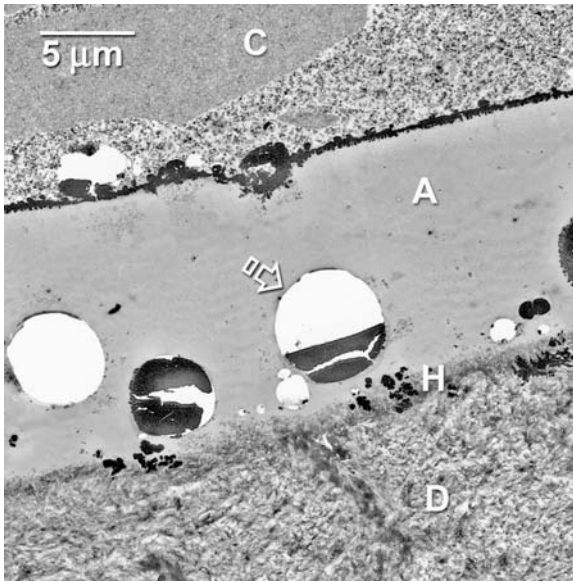
5.9 Severe water-treeing in an adhesive, occupying more than half the volume of the adhesive layer (A). This kind of severe fractal-like water-treeing was observed from thermomechanical stress of the adhesive interface created by the use of a single-bottle, one-step self-etch adhesive. C, composite; H, hybrid layer; D, dentine.



5.10 'Reflecting' or reverse water trees (asterisk) growing downward from a water layer (W) trapped between the first and second adhesive coats (A) of a one-step self-etch adhesive. (C, composite; H, hybrid layer; D, dentine.)

(Fig. 5.6). Apart from water trees, spherical water droplets could also be identified in HEMA-free, one-step self-etch adhesives (Fig. 5.11). These water droplets were surmised to be caused by phase separation of the water from the hydrophobic components following evaporation of the adhesive solvent (Van Landuyt *et al.*, 2005). HEMA is miscible with water in all proportions and is often utilized as a transitional, polymerizable solvent for other ionic resin monomers that are sparingly soluble in water. When HEMA is absent, phase separation of the adhesive components occurs. In contrast, when HEMA is present, the HEMA–water mixture polymerizes to form a hydrogel.

Unlike the water droplets in the aforementioned HEMA-free, one-step self-etch adhesives, which may be identified from intact, non-bonded adhesives before water sorption (King *et al.*, 2005), water trees are only observed when simplified dentine adhesives are applied to dentine. According to the 'water flux' theory of water-tree formation (Tay *et al.*, 2005a, 2005b), water trees are morphologic manifestations of water movement from the underlying dentine substrate into a partially polymerized adhesive resin matrix, in which the polymer chains are not sufficiently cross-linked to resist their displacement by the bulk free water.



5.11 Spherical water droplets (open arrow) scattered throughout the adhesive layer (A) of a HEMA-free, one-step self-etch adhesive. These water droplets represent phase separations of water from the more hydrophobic adhesive. (C, composite; H, hybrid layer; D, dentine.)

5.2.4 Source of water for water trees

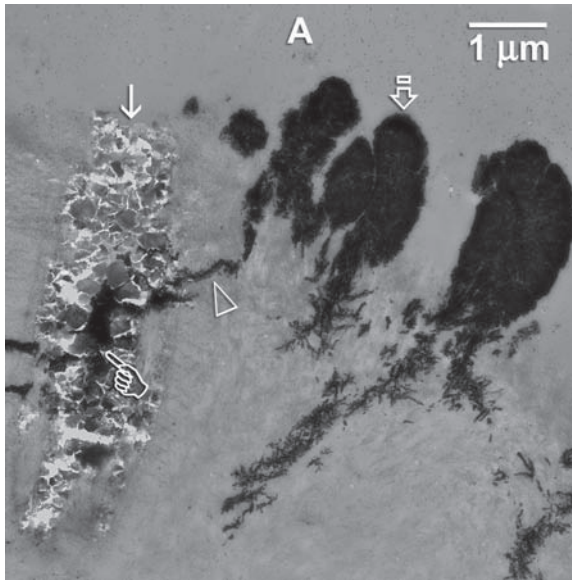
Three types of fluid movement may occur through the dentine: evaporative, osmotic and convective water fluxes. Convective water fluxes are considerably reduced when smear layers and smear plugs remain intact (such as during the application of mild self-etch adhesives), when vital acid-etched dentine is treated with glutaraldehyde-containing desensitizers to coagulate the plasma proteins in dentinal fluid (Schüpbach *et al.*, 1997), or when acid-etched dentine is treated with potassium oxalate salts to block the subsurface dentinal tubular orifices with calcium oxalate crystals (Pashley *et al.*, 2001; Pereira *et al.*, 2005). However, evaporative water flux may be induced by air blasts (Goodis *et al.*, 1990), such as those that occur during air-drying of a dentine adhesive. The presence of the smear layer and smear plugs offers little resistance to evaporative water loss. Dehydrating dentine with an air blast or with absorbent paper will generate capillary forces that induce rapid outward fluid movement from dentinal tubules (Matthews *et al.*, 1993). Similarly, the application of a porous water-based restorative material such as glass-ionomer cement does not completely eliminate evaporative water flux (Sidhu *et al.*, 2004). Because non-vital

dentine also contains water, evaporative water flux may occur irrespective of the tooth's vitality status, even when smear plugs are retained within the dentinal tubules. Although it is mandatory to remove adhesive solvents and water (Yiu *et al.*, 2005) from solvated adhesives before light-curing, the same air-drying process induces outward evaporative water flux from the smear-layer-covered dentine (Hashimoto *et al.*, 2004a). The high concentrations of water-soluble ionic monomers in the presence of water may also induce osmotic water flux from deep dentine if the osmolalities of these comonomers exceed the osmolality of dentinal fluid (Pashley *et al.*, 1992, 1996). The high solute concentrations in dentine adhesives as compared with the solute concentrations in dentinal fluid mean that the water concentration of dental adhesives is much lower than the water concentration in dentinal fluid, thus causing osmotic fluid movement from dentinal fluid into these concentrated comonomer films. When the monomers are converted to polymers the osmotically induced water flux should cease.

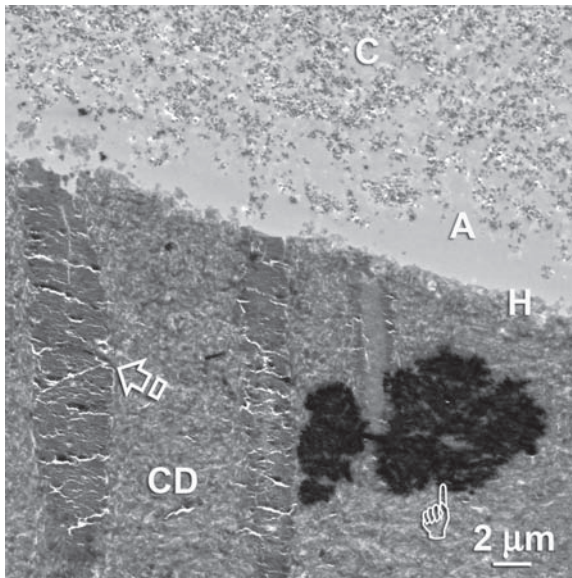
Both evaporative and osmotic fluxes may result in the permeation of water along regions within the adhesive where interchain segmental mobility is increased by hydrogen bonding of retained bound water with functional groups in polymers capable of hydrogen bonding. This provides a logical explanation for the predilection of water trees to be oriented perpendicular to the surface of the dentine. In particular, such a theory also accounts for the observation that in the presence of smear plugs or mildly sclerotic dentine (Fig. 5.12(a)), silver-containing tracks are observed around the peritubular dentine (i.e. the channels with the least resistance) that are continuous with silver-containing interfibrillar spaces in hybrid layers formed by mild self-etching primers. These nanoleakage tracks, in turn, are continuous with the vertically oriented water trees along the surface of the hybrid layers.

The support for the 'water flux' theory of nanoleakage and water-tree formation in simplified self-etch adhesives is based on work using these adhesives for bonding to caries-affected dentine. When resin bonding is performed on sound dentine with open dentinal tubules, it is difficult to determine whether the entrapped water that causes the formation of nanoleakage and water trees originates from water-containing self-etch adhesives (the 'remnant water theory'; Tay *et al.*, 2004b) or from the hydrated dentine. In order to differentiate residual water from permeating water, we selected impermeable dentine as a bonding substrate. Caries-affected dentine is heavily occluded with intratubular mineral deposits (Ogawa *et al.*, 1983; Silva *et al.*, 2006). Tubular occlusion accounts for the relative water impermeability of this type of bonding substrate (Tagami *et al.*, 1992). When convective and evaporative water fluxes are eliminated by bonding to transparent carious dentine (Lee *et al.*, 2003), any water entrapment

(a)



(b)



5.12 *a* Transmission electron micrograph of water-filled channels (now filled with silver); pointer followed by open arrowhead between a sclerotic dentine tubule (arrow) and peritubular dentine, that are continuous with silver-containing inter-fibrillar spaces in hybrid layers and with water trees (open arrow) extending into the adhesive layer in primary dentine; *b* Nanoleakage and water trees were absent from resin bonds made to caries-affected dentine (CD) because the tubules were heavily occluded with fine mineral crystals (open arrow). Note the extensive uptake of silver (pointer) into the caries-affected dentine beneath the hybrid layer (H). This is due to the high water content of caries-affected dentine, which has lost about half of its mineral phase and this phase has been replaced by water. (A, adhesive; C, composite.)

within the adhesive should be attributed to the retention of water derived from one-step self-etch adhesives. Surprisingly, despite the presence of heavy silver deposits in the subsurface porous caries-affected dentine, both nanoleakage and water trees that were seen in bonded sound primary dentine (Fig. 5.12a) were completely absent in primary caries-affected dentine (Fig. 5.12b). This demonstrates that the source of the water in water trees is water from dentinal tubules, not residual water from the self-etching adhesive.

The absence of interfacial nanoleakage following the use of self-etch adhesives in transparent carious dentine provides reassurance of the validity of the concept of simultaneous etching and priming in self-etch adhesives. Although tubular occlusion by mineral crystals prevents water-treeing and nanoleakage in one-step self-etch adhesives, it is unrealistic clinically to assume that one can bond only to transparent carious dentine without involving surrounding sound dentine. Unlike the use of etch-and-rinse adhesives in which the dentinal tubules can first be occluded with mineral deposits such as calcium oxalate before bonding (Pashley *et al.*, 2001; Yiu *et al.*, 2006a), such a protocol is not applicable to the application of one-step self-etch adhesives. At least from an *in vitro* aspect, improvements in bond strength and reductions in nanoleakage and water-tree formation may be achieved when multiple coats of one-step self-etch adhesives are used on sound dentine, instead of the limited number of coats that are recommended by manufacturers (Ito *et al.*, 2005a). Such a technique, however, cannot reduce subsequent water sorption by these adhesives, as they are by nature highly hydrophilic. Alternatively, one-step self-etch adhesives can be rendered less permeable by treating the one-step self-etch adhesive as a primer and covering it with a less hydrophilic resin coating such as those that are employed in conventional etch-and-rinse adhesives. This extra step converts one-step into two-step self-etch adhesives (Brackett *et al.*, 2005; King *et al.*, 2005; Van Landuyt *et al.*, 2006) and renders them less permeable to water movement.

The susceptibility of highly hydrophilic adhesives to water sorption, and the existence of potential water channels that expedited water sorption when simplified versions of these adhesives are bonded to dentine, were demonstrated when Class II resin composite restorations were challenged under functional stresses (Frankenberger *et al.*, 2005). Although high percentages of gap-free margins were initially identified in enamel for all the four classes of adhesives before *in vitro* thermomechanical loading, etch-and-rinse adhesives exhibited significantly higher percentages of gap-free margins (approximately 90%) when compared with two-step self-etch adhesives (approximately 75%) and one-step self-etch adhesives (approximately 55%), after thermomechanical cycling. For dentine, 89–100% gap-free margins were initially observed for all adhesives. After

thermomechanical cycling, there were no statistical differences among etch-and-rinse (62–70%) and two-step self-etch (62–63%) adhesives. However, the one-step self-etch adhesives exhibited significantly fewer gap-free margins (15–40%).

5.3 Permeability of dentine

5.3.1 Permeation of intratubular versus intertubular dentine

There are two different types of dentine permeability: permeation of solutes and solvents across dentine via dentinal tubules, the so-called ‘intratubular permeability’, and permeation of solutes and solvents into but not through dentine. The former permeability is responsible for dentine sensitivity, while the latter is responsible for water permeation during dentine bonding. These two different types of dentine permeability are sometimes inter-related. That is, if during dentine bonding, adhesive resins do not seal dentinal tubules, then ‘bonded dentine’ may become sensitive. We will begin this section of the review by discussing monomer permeation into intertubular dentine.

Mineralized dentine is not very porous except for the presence of dentinal tubules. If adhesive monomers are applied to mineralized dentine, the amount of monomer uptake is very small (Pashley *et al.*, 2000) and resin–dentine bond strength is very low (Gwinnett, 1993) because the only continuity between dentine and the overlying resin is the presence of resin tags if the dentine was fractured (i.e. smear-layer free). Grinding dentine creates smear plugs and smear layers that prevent resin tag formation (Brännström, 1984; Pashley, 1984). Early adhesive products such as Scotchbond Dual Cure were applied directly to smear-layer-covered dentine. The resin was unable to penetrate through the smear layer and hence gave very low bond strengths (c. 5–10 MPa). Examination of both sides of the failed resin–dentine bonds revealed smear-layer material on both sides. Thus, the ‘bond strength’ was not really a measure of bonding, but measured the cohesive strength of the smear layer that split into upper and lower halves (Tao *et al.*, 1988).

5.3.2 Contribution of resin infiltration to resin–dentine bond strength

It became clear that if resin–dentine bond strengths were to improve, the smear layers would have to be partially or fully removed along with the underlying smear plugs that prevented resin tag formation (Gwinnett, 1993). However, even smear-layer removal was insufficient for high

resin–dentine bond strength. What was required was stripping the mineral phase from the collagen fibrillar matrix of dentine to produce a large increase in surface and subsurface porosity. Using weak acids, the top 5–10 μm of the dentine surface could be stripped free of apatite crystallites to expose the collagen fibril mesh. If monomers could flow into this meshwork and coat the fibrils with polymerized resin to provide micromechanical retention, they would produce high bond strengths. When HEMA uptake into mineralized dentine was compared with HEMA uptake into acid-etched dentine, the mineralized matrix only took up 4% as much as the etched matrix (Pashley *et al.*, 2000). This confirmed, in quantitative terms, what Nakabayashi *et al.* (1982) demonstrated qualitatively. Their 1982 report of how monomers could be coaxed into a demineralized dentine matrix was revolutionary. Although Buonocore (1955) had demonstrated how resins could be bonded to enamel, it was really Kramer and McLean (1952) and later Nakabayashi *et al.* (1982) who demonstrated that adhesive resins could penetrate into etched dentine. Nakabayashi and his colleagues were the first to use TEM techniques that had sufficient resolution to show that the demineralized zone of the dentine matrix became infiltrated with resin to create an entirely new biomaterial that was half collagen fibrils and half resin. It was neither resin nor dentine but a hybrid of the two (Nakabayashi and Pashley, 1998), hence the term, the ‘hybrid layer’.

When hybrid layers were first described (Nakabayashi *et al.*, 1982; Inokoshi *et al.*, 1990; Van Meerbeek *et al.*, 1992), many clinicians believed that the mechanism of bonding had been revealed in its entirety. Instead, the complexities of bonding became apparent when the same adhesive products produced hybrid layers of different thicknesses depending on dentine depth and dentine condition (i.e. normal vs. caries-affected).

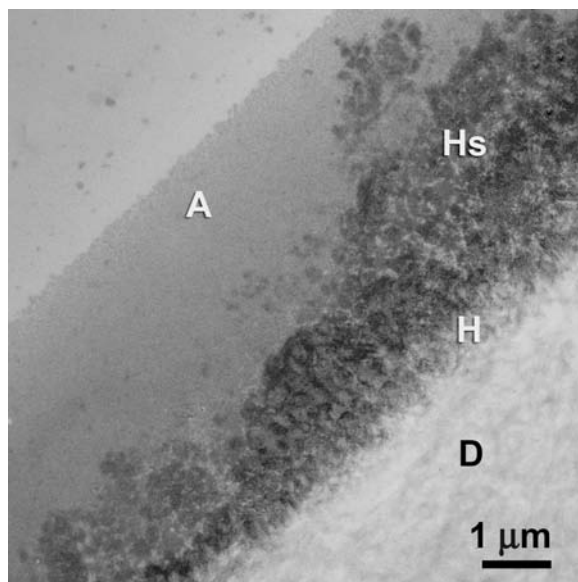
When it was discovered that acid-etching lowered the stiffness of dentine from 18000 MPa to 1–5 MPa (Maciel *et al.*, 1996; Eddleston *et al.*, 2003), the susceptibility of the demineralized matrix to collapse became apparent. It was discovered that even after primer infiltration (35% HEMA in 65% water) into the matrix, the matrix was so compliant that evaporation of solvent was enough to cause it to collapse and extrude much of the monomers it had taken up (Eddleston *et al.*, 2003). The use of ethanol-solvated primer mixtures stiffened the matrix enough to lower, but not prevent, matrix collapse (Agee *et al.*, 2006; Becker *et al.*, 2007; Pashley *et al.*, 2007). The kinetics of monomer infiltration, solvent evaporation and the degree of matrix collapse could not be measured in microscopic hybrid layers using currently available technology. This led to the development of what has been called the ‘macro-model of the hybrid layer’ (Pashley *et al.*, 2007) to permit quantitative measurements of the permeability of the dentine matrix.

5.3.3 Permeability of smear layers to acidic adhesives

The recent development of self-etching adhesives revolutionized adhesive dentistry. This was accomplished by adding 20–30% acidic methacrylates (pH 1.9–2.8) to 20% water, 20% ethanol, 30% HEMA or dimethacrylates. The acidic methacrylates can only dissociate in the presence of water. Acids do not dissociate to form H^+ , but rather form hydronium ions with water (H_3O^+). The presence of water requires the use of water-miscible hydrophilic comonomers (e.g. HEMA) and/or acetone or ethanol as a solvent to prevent phase changes from occurring (Spencer and Wang, 2002; Van Landuyt *et al.*, 2005).

Self-etching adhesives are applied directly to smear-layer-covered dentine under dry conditions, since they contain their own water. They are acidic enough to etch through smear layers or at least demineralize the smear layer via water-filled interfibrillar spaces (Pashley *et al.*, 1992). Although agitation or scrubbing of smear layers with self-etching adhesives can completely remove thick smear layers (Chan *et al.*, 2003), that option is not always possible in complex cavity preparations where the adhesive layer may remain passive during the 20s etch. Self-etching systems easily penetrate 1–2 μm of smear layers but only penetrate about 0.5 μm into the underlying mineralized dentine (Fig. 5.13). This is due, in part, to the fact that the acidity is partially buffered by the smear layer during comonomer penetration (Reis *et al.*, 2005), and because the underlying mineralized dentine is less porous, and hence less permeable, than smear layers. Unlike etch-and-rinse adhesives, self-etching adhesives are not rinsed. The calcium and phosphate ions that are liberated from apatite crystallites during self-etching, presumably dissolve in the water of the adhesive blend. Some of the calcium ions associate with the acidic monomers as calcium salts. That mixture fills interfibrillar spaces and some of those ions may diffuse up into the overlying adhesive layer. After etching for 20s, the reaction is ‘terminated’ by evaporating the solvents including water. Any free calcium and phosphate ions in that water presumably precipitate as calcium phosphates, which become dispersed within the comonomers in the interfibrillar spaces (Bayle *et al.*, 2007).

Not all self-etching adhesives are equally effective. There are two major classes of self-etching adhesives: self-etching primer adhesives where the acid primer-treated dentine is covered with solvent-free more hydrophobic adhesive; and self-etching adhesives that are not covered with solvent-free more hydrophobic adhesive resins. Examples of the former include Clearfil Liner Bond 2V and SE Bond (Kuraray Medical Inc.), Fluorobond (Shofu) and Unifil Bond (GC Corp.). Examples of the latter include Adper Prompt L-Pop (3M, ESPE), iBond (Heraeus Kulzer), G-Bond (GC Corp.) and Xeno IV (Dentsply).



5.13 Transmission electron micrograph showing a mild self-etching adhesive (A) penetrating through 1–2 μm thick smear layers (Hs), but only penetrating 0.5 μm to form a hybrid layer (H) in the underlying intact dentine (D).

5.3.4 Permeability of resin-bonded dentine to water

When hydrophilic and hydrophobic monomers are mixed, as in the case of one-step self-etch adhesives, the resulting resin films behave as hydrophilic resins (Itthagarun *et al.*, 2004). In contrast, when hydrophobic coatings are made over hydrophilic resins, the combination behaves as if it were hydrophobic (Brackett *et al.*, 2005; King *et al.*, 2005). Apparently, when hydrophilic and hydrophobic monomers are mixed together, hydrophilic phases or domains extend across the entire adhesive resin layer that permit not only nanoleakage but bulk-water movement across the resin-bonded dentine (Tay *et al.*, 2003b; Chersoni *et al.*, 2004; Sauro *et al.*, 2006, 2007). In the latter paper, the number of water droplets per unit area was shown to correlate very well with quantitative fluid permeability. Thus, evidence is accumulating that demonstrates that the use of solvated mixtures of hydrophilic and hydrophobic monomers for resin–dentine bonding creates polymerized resin coatings that are permeable to water.

Although the permeability properties of adhesive resins can be studied independently of dentine (Hashimoto *et al.*, 2005), they are best studied together because the resin–dentine interface is the critical functional unit (Hashimoto *et al.*, 2004b; Spencer *et al.*, 2006).

5.4 Hydrophilic versus hydrophobic properties of resins

5.4.1 Use of Hoy's solubility parameters to rank hydrophilicity

Although the terms 'hydrophilicity' (i.e. water loving) and 'hydrophobicity' (i.e. water hating) are commonly used, they are seldom defined in quantitative terms. Solubility parameter theory has been shown to be very useful in quantitating or ranking degrees of hydrophilicity of polymers. In dentistry, the first use of solubility parameters was by Asmussen and his colleagues. They were also the first to regard demineralized collagen as a porous solid polymer. They reasoned that for primers to penetrate demineralized dentine, the primers should have a solubility parameter that is very similar to the polymeric substrate, as is true in general in polymer chemistry (Asmussen *et al.*, 1991; Asmussen and Uno, 1993; Finger *et al.*, 1994). They found that the higher the Hildebrand solubility parameter of their primers, the thicker were the hybrid layers. This concept was expanded by Miller (1995) and by Miller *et al.* (1998) using Hansen's triple solubility parameters to calculate the relative contribution of dispersion cohesive forces (δ_d), polar cohesive forces (δ_p), hydrogen bonding forces (δ_h) and the total cohesive forces of adhesives (δ_t). Miller's other major contribution was the calculation of Hansen's solubility parameters for dentine collagen, assuming a water content of 30 wt%. He summed the molar attractive constants of the functional groups of all the amino acids in collagen. The details of how this is done can be found in previously published work (Miller, 1995; Agee *et al.*, 2006). Since manufacturers are unwilling to divulge the exact chemical composition of their adhesives, the solubility parameters of their adhesive cannot be calculated. In order to avoid this problem, Pashley *et al.* (2007) formulated five resin blends of known composition, that range from hydrophobic to mildly hydrophilic to very hydrophilic (Table 5.1). As Hoy's triple solubility parameters are more widely used (Barton, 1991), Table 5.2 shows how chemical structures modify the calculated Hoy's solubility parameters for dispersive forces (δ_d), polar forces (δ_p), hydrogen bonding forces (δ_h) and total cohesive forces (δ_t). Miller (1995) calculated an interpeptide hydrogen bonding force (δ_h) of dentine collagen of $23.6 \text{ (J/cm}^3)^{1/2}$ for a 30% water–70% collagen peptide mixture. That is a good estimate for water-saturated collagen matrices but not for dried matrices (Table 5.1). We calculated a Hoy's δ_h value of $14.8 \text{ (J/cm}^3)^{1/2}$ for 0% water–100% collagen peptides (Agee *et al.*, 2006). This is an estimate of the 'strength' of interpeptide hydrogen bonding that occurs when acid-etched dentine is air-dried. These hydrogen bonding forces actively collapse the matrix, bringing collagen peptides close together. This causes a loss of interfibrillar spaces

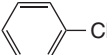
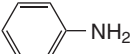
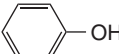
Table 5.1 Composition of neat experimental resins 1 to 5 and Hoy's solubility parameters for the solvated comonomers and for demineralized dentine (collagen)

Resin no.	Resin composition	Hoy's solubility parameters [(J/cm ³) ^{1/2}]			
		δ_d	δ_p	δ_h	δ_t
1	70 wt% E-BisADM; 28.75% TEGDMA; 1.0% EDMAB; 0.25% CQ	15.0	10.3	6.6	19.4
2	70% BisGMA; 28.75% TEGDMA; 1.0% EDMAB; 0.25% CQ	15.9	12.4	6.5	21.2
3	70% BisGMA; 28.75% HEMA; 1.0% EDMAB; 0.25% CQ	15.6	13.0	8.5	22.1
4	40% BisGMA; 30% TCDM; 28.75% TEGDMA; 1.0% EDMAB; 0.25% CQ	16.5	12.9	7.0	22.1
5	40% BisGMA; 30% BisMP; 28.75% HEMA; 1.0% EDMAB; 0.25% CQ	15.1	13.5	11.1	23.1
Collagen	30% water, 70% peptides	11.8	15.3	22.5	30.1
Collagen	30% ethanol, 70% peptides	12.0	12.5	18.1	25.1
Collagen	0% water, 100% peptides	11.7	12.1	14.8	22.5
Ethanol		12.6	11.2	20.0	26.1
Water		12.2	22.8	40.4	48.0

All Hoy's solubility parameters were calculated using commercially available software (Computer Chemistry Consultancy: www.compchemconsul.com). δ_d , Hoy's solubility parameter for dispersive forces; δ_p , Hoy's solubility parameter for polar forces; δ_h , Hoy's solubility parameter for hydrogen bonding forces; δ_t , Hoy's solubility parameter for the total cohesive forces, that is equivalent to Hildebrand's solubility parameter, $\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$.

Abbreviations: BisGMA, 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)]-phenyl propane; TEGDMA, triethylene glycol dimethacrylate; EDMAB, 2-ethyl dimethyl-4-aminobenzoate; CQ, camphorquinone; E-BisADM, ethoxylated bisphenol A diglycidyl methacrylate; HEMA, 2-hydroxyethyl methacrylate; TCDM, di(hydroxyethylmethacrylate)ester of 5-(2,5,-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexane-1,2'-dicarboxylic acid; BisMP, bis[2-(methacryloyloxy) ethyl] phosphate (Pashley *et al.*, 2007).

Table 5.2 Hoy's solubility parameters for nonpolar versus polar solvents

Structure	Solution	δ_d	δ_p	δ_h
	Benzene	16.1	0.0	0.0
	Chlorobenzene	17.4	9.4	0.0
	Aniline	19.4	5.1	7.2
	Phenol	18.0	5.9	14.9
$\text{CH}_3-(\text{CH}_2)_5-\text{OH}$	Hexanol	15.0	8.5	13.7
HOH	Water	12.2	22.8	40.4

δ_d , Hoy's solubility parameter for dispersion forces; δ_p , Hoy's solubility parameter for polar forces; δ_h , Hoy's solubility parameters for hydrogen bonding forces; all in $(\text{J}/\text{cm}^3)^{1/2}$ (Pashley *et al.*, 2007).

which are necessary for monomer penetration during bonding. These forces, if allowed to develop, also produce large increases in matrix stiffness (Maciel *et al.*, 1996; Eddleston *et al.*, 2003; Pashley *et al.*, 2007). Thus, if the acid-etched dentine matrix is air-dried, it becomes stiff and compact due to spontaneous formation of interpeptide hydrogen bonds. When collagen takes up water, the water breaks interpeptide hydrogen bonds because water has a much higher δ_h value of $40 (\text{J}/\text{cm}^3)^{1/2}$ compared with the $14.8 (\text{J}/\text{cm}^3)^{1/2}$ value for interpeptide hydrogen bonds. The collagen re-expands as water 'plasticizes' the biopolymer, thereby opening up interfibrillar spaces for resin uptake (Becker *et al.*, 2007). In this expanded state that is obtained during wet bonding, the interfibrillar spaces are completely filled with water. Unfortunately, many adhesive monomers are not very soluble in water. That is why marketed adhesives are usually solvated in ethanol or acetone. When solvated adhesives are placed on water-saturated acid-etched dentine, their solvents try to diffuse into the water-filled spaces and some of the water in the spaces diffuses into the solvent. This results in too little solvent remaining in the infiltrating adhesive to keep BisGMA in solution. The net result is incomplete penetration of BisGMA into water-saturated matrices (Spencer and Wang, 2002). When BisGMA-HEMA mixtures are placed on water-saturated dentine, the applied concentration changes as the much more water-soluble HEMA diffuses to the base of the demineralized zone, tending to enrich the surface concentration of BisGMA. This has been considered as an example of molecular sieving, perhaps due to the presence of proteoglycan hydrogels in the interfibrillar space.

Alternatively, the same results might be explained by differential monomer solubility in the ‘final solvent’ in the interfibrillar spaces. The initial solvent is water, but during bonding some water is replaced by some ethanol or other adhesive solvent; the exact composition of the final state is unknown but probably contains too much water for BisGMA to remain soluble. However, the width of interfibrillar spaces is only 20–30 nm. This may be too small for phase changes to be seen by even scanning electron microscopy (SEM) or TEM. This problem can be avoided by replacing water in the matrix by 100% ethanol. As the volume of ethanol applied to the matrix is far in excess of the amount of water in the matrix, the water in the interfibrillar spaces rapidly diffuses into the ethanol. BisGMA and other dimethacrylates are very soluble in ethanol, therefore there are no phase changes or solubility issues (Pashley *et al.*, 2007).

5.4.2 Wet bonding with water- or ethanol-saturated dentine

We believe that many single-bottle etch-and-rinse adhesives are too hydrophilic (Tay and Pashley, 2003b). That is, they contain too much HEMA and other hydrophilic monomers that create hydrophilic copolymers. The hydrophilic polymers attract too much water which causes swelling of resins that are plasticized by water uptake, thereby reducing their mechanical properties. If more hydrophobic resins such as BisGMA and TEGDMA could be coaxed to coat collagen fibrils during resin bonding, they would absorb much less water and may seal collagen fibrils from water, thereby slowing or preventing enzyme-catalyzed hydrolytic cleavage of collagen. The problem is that BisGMA and TEGDMA have poor water solubilities.

However, the recent development of a new bonding technique called ‘ethanol-wet bonding’, replaces the water in acid-etched dentine with 100% ethanol just before bonding. We speculate that this permits BisGMA/TEGDMA mixtures to infiltrate deep into the hybrid layer without undergoing phase changes (Nishitani *et al.*, 2006b; Pashley *et al.*, 2007; Sadek *et al.*, 2007). Replacement of water by ethanol increases the bond strength of most hydrophobic resins including BisGMA/TEGDMA mixtures by bringing the Hoy’s solubility parameter for total cohesive forces (δ_t) of the ethanol-saturated matrix very close to that of ethanol-solvated BisGMA/TEGDMA mixtures. The δ_t values of water-saturated mixtures are too far away from the δ_t of BisGMA/TEGDMA indicating that the solvated comonomers are not miscible with water-wet bonding (Pashley *et al.*, 2007; Sadek *et al.*, 2007).

The use of water-free polar solvents is not new, since many bonding systems have used acetone as the solvent. However, the high vapor pressure of acetone causes it to evaporate too quickly. Ethanol does not evaporate

as fast as acetone does, providing more time in residence to chemically dehydrate the matrix of water before comonomer infiltration.

5.4.3 Influence of solvents versus monomers on resin penetration

As ethanol (Hoy's $\delta_h = 20$) replaces water ($\delta_h = 40$), the collagen matrix will spontaneously develop some interpeptide hydrogen bonds because the δ_h value of ethanol is closer to the δ_h value of $14.8 \text{ (J/cm}^3)^{1/2}$ of the collagen peptides than that of water. Hydrogen-bond formation depends on probability. In water-saturated collagen matrices ($\delta_h = 40$), the probability of forming interpeptide hydrogen bonds between adjacent collagen peptides with a δ_h of 14.8 is zero. In ethanol-saturated matrices, there is a higher probability at any instant, some adjacent peptides will develop interpeptide hydrogen bonds, while most of those peptide groups capable of hydrogen bonding will be hydrogen bonding with ethanol instead of themselves. This slight tendency to form interpeptide hydrogen bonding causes a small (c. 16–18%) shrinkage of the demineralized dentine matrix (Pashley *et al.*, 2007). This shrinkage is a small price to pay for filling the matrix spaces with an excellent polar solvent for adhesive monomers that is volatile enough to be evaporated by an air-syringe but not so volatile that it evaporates before monomer infiltration is complete.

In polymer chemistry, an important rule is that solutions with similar solubility parameters (i.e., δ , the solubility parameter for total cohesive forces) are miscible. A corollary to that rule is that solutions with similar solubility parameters (i.e. δ) to those of polymers, can permeate those polymers, causing them to swell. Generally, 'similar' means that the differences between the solvents or solvents and polymers do not exceed $5 \text{ (J/cm}^3)^{1/2}$. Table 5.1 lists the Hoy's solubility parameters for common dental adhesives and for dry collagen vs. water- and ethanol-saturated collagen and for ethanol.

Dry collagen is relatively hydrophobic (Table 5.1), if that term is defined as a substance with a δ_t value of $25 \text{ (J/cm}^3)^{1/2}$. Water-saturated collagen (30% water–70% collagen) is more hydrophilic if we define that term as a substance having a δ_t value $> 25 \text{ (J/cm}^3)^{1/2}$. That is, the δ_t of dry collagen is $22.5 \text{ (J/cm}^3)^{1/2}$ while that of water-wet collagen is $30.1 \text{ (J/cm}^3)^{1/2}$. The 'hydrophilicity' of water-wet collagen is due to its water content, not the collagen itself, because water (Table 5.1) has such a high δ_t of $48 \text{ (J/cm}^3)^{1/2}$. BisGMA, with a δ_t of $22.0 \text{ (J/cm}^3)^{1/2}$ is $8.1 \text{ (J/cm}^3)^{1/2}$ away from that of water-saturated collagen ($\delta_t = 30.1 \text{ (J/cm}^3)^{1/2}$); but is only 4.1 units away from ethanol-saturated collagen ($\delta_t = 22.5 \text{ (J/cm}^3)^{1/2}$), hence BisGMA should be soluble in ethanol-saturated collagen. Because BisGMA molecules hydrogen-bond to themselves, their effective molecular weight is a multiple of the true

molecular weight, causing undiluted BisGMA to have such a high viscosity that it can not be expected to diffuse into dentine matrices. This is why BisGMA is usually mixed with HEMA or TEGDMA which serve as diluents. We prefer TEGDMA as a diluent because it is more hydrophobic than HEMA and hence absorbs less water (Ito *et al.*, 2005b; Malacarne *et al.*, 2006). Ethanol can also be used as a diluent for BisGMA (Tay *et al.*, 2007).

Thus, solubility parameter theory is very useful in predicting how miscible monomers should be in demineralized matrices saturated with various solvents (Pashley *et al.*, 2007; Sadek *et al.*, 2007). The above discussion also provides the rationale for the use of Hoy's solubility parameters for ranking the degree of hydrophilicity or hydrophobicity of monomers or monomer–solvent mixtures.

5.4.4 Effects of water sorption on mechanical properties of resins

The five model adhesives shown in Table 5.1 represent a spectrum of resin blends from relatively hydrophobic to relatively hydrophilic. Resins 1 and 2 represent non-solvated hydrophobic adhesives that are used in the final step of three-step etch-and-rinse adhesives or pit-and-fissure sealants. Resin 3 is somewhat hydrophilic and represents typical single-bottle etch-and-rinse adhesives. Resins 4 and 5 are acidic comonomers due to the presence of carboxylic acid or phosphoric acid methacrylate derivatives, respectively, making them more polar and more ionic than resins 1 to 3. In a recent paper (Ito *et al.*, 2005b), these experimental adhesives were used to measure water sorption, solubility and changes in the modulus of elasticity of the disks during immersion in water vs. oil (i.e. hexadecane) over time. When immersed in oil, there was no significant decrease in the modulus of elasticity of the polymers over three days. In contrast, when the same experimental adhesives were immersed in water, they showed significant decreases in moduli of elasticity that correlated with their δ_p values. The higher the δ_p , the higher the water sorption; the higher the water sorption, the lower the moduli of elasticity. Clearly, water, but not hexadecane, could be taken up by the polymer blends, which, in turn, plasticized the polymers making them lose up to 42% of their stiffness in only three days. This use of resin disks with two free surfaces overestimates the likely rate of water sorption that might occur in resin–dentine bonds where the adhesives are covered by mineralized dentine below and resin composite above, but it demonstrates the principle.

In a related paper (Nishitani *et al.*, 2007), we formulated a series of phenyl-P-based acidic primers containing varying amounts of BisGMA/TEGDMA and HEMA as well as a constant phenyl-P concentration. Note from Table 5.3, that phenyl-P is one of the most hydrophilic of dental

adhesive monomers ($\delta_t = 27.4 \text{ (J/cm}^3)^{1/2}$). Thus, these model primers were very hydrophilic and absorbed water in proportion to their hydrophilicities (Fig. 5.14a; Table 5.4). When we combined the Ito *et al.* (2005b) water sorption data with the Nishitani *et al.* (2007) water sorptions vs. δ_h values, we obtained highly significant correlations (Fig. 5.14b). In this combined data set, one can predict water sorption of polymers from their Hoy's δ_t values.

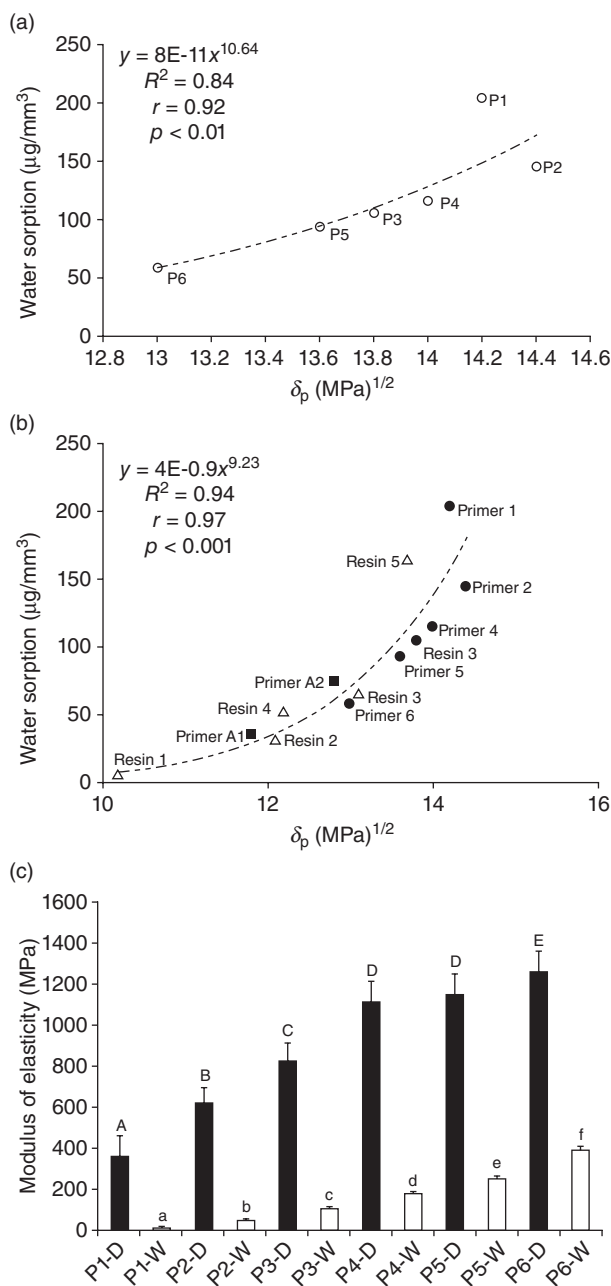
There was also a significant correlation between the composition of these acidic primers and their modulus of elasticity (Hosaka *et al.*, 2007). That is, the higher the BisGMA/TEGDMA content, the higher the moduli of elasticity (Fig. 5.14c). Using three-point bending of beams of these primer polymers, the stiffness of these dry polymers was shown to be inversely related to the δ_p of the polymer blend, to a greater extent than the δ_h values were. Polar groups like the phosphate group in phenyl-P would tend to attract monovalent cations as counterions along with water sorption, making these polymers very hydrophilic. The remarkable observation in that work was the large differences in stiffness of these polymers when they were tested dry vs. wet (Hosaka *et al.*, 2007). This was also reported by Yiu *et al.* (2004) when the ultimate tensile strength (UTS) of resins 1 to 5 were tested before and after water vs. oil immersion. After oil immersion, there was no decrease in the UTS of any of the resins. In contrast, after water immersion, there was a decrease in UTS that was proportional to the δ_h values of the resin (Fig. 5.15). That is, the higher the δ_h , the larger the fall in UTS, in a manner similar to that reported by Hosaka *et al.* (2007).

The same result has been shown in demineralized dentine matrices. Dry matrices are very stiff (c. 120 MPa) because there is maximal interpeptide hydrogen bonding (Fig. 5.16). However, within minutes after the addition of water, the collagen matrix becomes plasticized by water and the

Table 5.3 Hoy's solubility parameters of dry collagen and of common adhesive monomers

Concentration	Substance	δ_d	δ_p	δ_h	δ_t
Neat	BisGMA	15.6	12.5	9.4	22.0
Neat	HEMA	14.8	14.4	11.5	23.6
Neat	2-MP	16.9	17.0	12.1	26.8
Neat	Phenyl-P	17.6	17.1	12.2	27.4
Neat	MDP	17.9	13.0	8.7	23.4
Neat	TEGDMA	15.6	11.2	7.0	20.4
Neat	Dry collagen	11.7	12.1	14.8	22.5

2-MP, bis [2-(methacryloyloxy)ethyl] phosphate; MDP, 10-methacryloyloxy decamethylene phosphate acid.

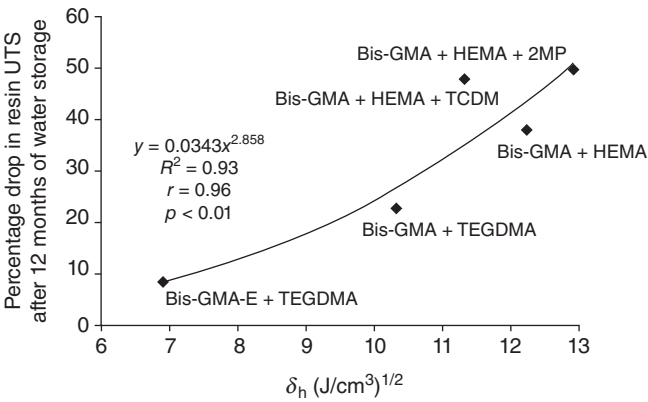


5.14 *a* Plot of increasing water sorption of a series of increasingly hydrophilic blends of phenyl-P-containing acidic primer polymers. *b* Same data combined with water sorptions of less hydrophilic primers. *c* Bar graph of the modulus of elasticity of phenyl-P polymers, when tested dry (-D) vs. after water sorption (-W). Different upper and lower case letters over the bars indicate they are statistically significantly different ($P < 0.05$).

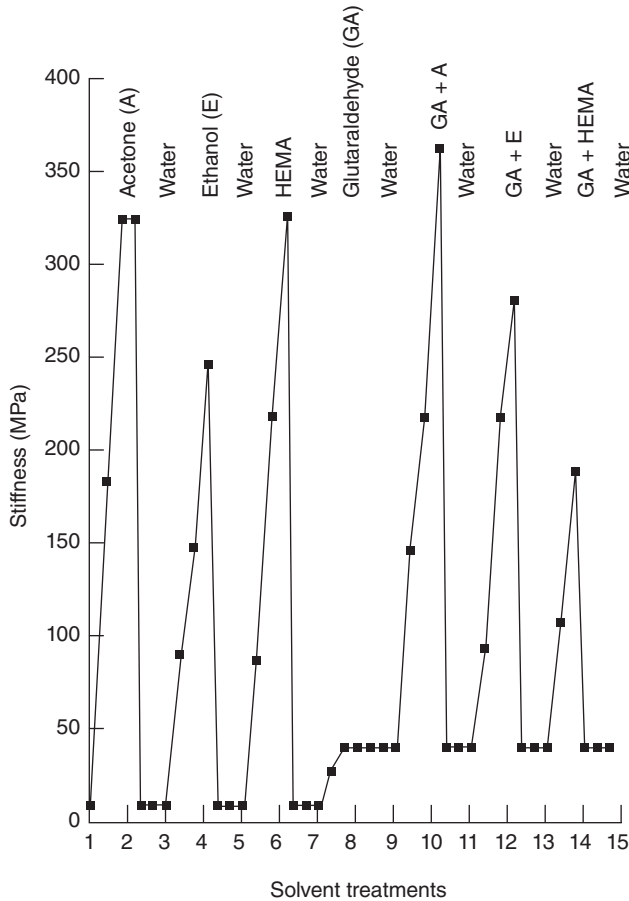
Table 5.4 Chemical composition and Hoy’s solubility parameters of test primer (P1 to P6)

Code	Monomer composition (wt%)				Hoy’s solubility parameters [(J/cm ³) ^{1/2}]			
	Phenyl-P	HEMA	BisGMA	TEGDMA	δ_d	δ_p	δ_h	δ_t
P1	20	56	—	24	15.5	14.2	10.6	23.5
P2	20	56	12	12	15.5	14.3	10.9	23.8
P3	20	40	12	28	15.7	13.8	10.1	23.2
P4	20	40	20	20	15.7	13.9	10.3	23.4
P5	20	24	28	28	15.8	13.5	9.8	23.0
P6	20	—	40	40	15.9	11.8	8.7	22.3

Hoy’s solubility parameters: δ_d , dispersive forces; δ_p , polar forces; δ_h , hydrogen bonding forces; δ_t , total cohesive forces (equivalent to Hildebrand’s δ). All primers (P) contained 20% water, 20% ethanol, 60% comonomers before evaporation. All primers contained 0.5% CQ and 1.0% EDMAB. Abbreviations: phenyl-P, 2-methacryloyloxyethyl phenyl phosphoric acid; HEMA, 2-hydroxyethyl methacrylate; BisGMA, 2,2-bis[4-(2-hydroxy-3-methacryloyloxy)]-phenyl propane; TEGDMA, triethylene glycol dimethacrylate; EDMAB, 2-ethyl dimethyl-4-aminobenzoate; CQ, camphorquinone.



5.15 Plots of the percentage decrease in the ultimate tensile strength (UTS) of increasingly hydrophilic experimental resins 1 to 5 versus their Hoy’s solubility parameter for hydrogen bonding cohesive forces (δ_h) in oil for 12 months (Yiu *et al.*, 2004).



5.16 Plot of changes in the stiffness of demineralized dentine beams when they were sequentially exposed to acetone, water, ethanol, HEMA, glutaraldehyde, etc. for 10, 30 and 60 min each. Note how rapidly water reversed the stiffness (Maciel *et al.*, 1996).

stiffness falls to about 10 MPa (Maciel *et al.*, 1996; Pashley *et al.*, 2007). The plasticization of the dentine matrix is much faster than that of polymers because the dentine matrix is so much more porous and permeable than resin matrices.

5.4.5 Reasons for the lack of durability of resin–dentine bonds

Resin–dentine bonds are composed of resins bonded to a demineralized dentine matrix. Anything that weakens either component should weaken

the bond strength. Clearly, the more hydrophilic the resins, the more water the polymers absorb, the more the polymer becomes plasticized and the polymers lose their mechanical properties. Thus, water plasticization of resins (Carrilho *et al.*, 2005a, 2005b; Ito *et al.*, 2005b; Hosaka *et al.*, 2007; Nishitani *et al.*, 2007) contributes to the decrease in durability of resin–dentine bonds.

Now that we know how to coax both hydrophilic and hydrophobic resins into acid-etched dentine saturated with ethanol, why should we continue to use hydrophilic comonomer blends? They are absolutely necessary for self-etching adhesives because water is required to ionize the acidic monomers so that they will etch through smear layers into the underlying hard tissues. Water is also helpful for solubilizing the calcium and phosphate ions that are liberated by the etching. Thus, for self-etching systems, water is a necessary ingredient and requires the use of hydrophilic resin blends. This was not a problem in self-etching primer adhesive systems where the dried hydrophilic primer was covered with a separate, solvent-free, more hydrophobic adhesive that sealed the hydrophilic primer with a hydrophobic surface seal. This is not done in self-etching, all-in-one, single-bottle systems. In such systems, water and hydrophilic and hydrophobic resins are all mixed in the same bottle. They are homogenized to keep them in a single phase. When applied to dentine, the homogenized coating behaves as if it contains extremely hydrophilic sites that allow water to permeate the layer (Tay *et al.*, 2004a, 2004c, 2004d). Bond strengths are rather low, nanoleakage is high and the bonds are not very durable. For etch-and-rinse adhesives, it would seem that ethanol-wet bonding using relatively hydrophobic resins would strengthen the resin side of resin–dentine bonds by preventing the loss of mechanical properties that is seen in hydrophilic polymers following water sorption. However, this prediction needs to be demonstrated as valid. There are as yet no long-term *in vitro* or *in vivo* studies showing that resin–dentine bonds made with hydrophobic resins are more durable over time (i.e. show less decrease in bond strength over time).

The second component of resin–dentine bonds, the demineralized dentine matrix, may be less stable than previously thought due to the presence of endogenous matrix metalloproteinases (MMPs) in dentine (Martin De Las Heras, 2000; Mazzoni *et al.*, 2007; Sulkala *et al.*, 2007). We are unaware of any connective tissue in the body that contains type I collagen that does not also contain MMPs designed to hydrolyze the very substrate to which they are bound. In soft tissues, these collagenases are either secreted in a latent or proform, or inhibited by tissue inhibitors of metalloproteinases (TIMPs). In mineralized tissues, these enzymes may be active, secreted in a proform or inhibited by TIMPs as well as being covered by apatite crystallites that fossilize the enzymes to block their activity. However, these crystallites are stripped away from the collagen and all of its bound proteins

including MMPs during acid-etching. This may, under many circumstances, activate these enzymes so that they can slowly, over many months, attack any collagen fibrils that are not enveloped by adhesive resin. They may even attack collagen fibrils covered by resins, especially hydrophilic resins that promote water uptake. The evidence for this will be covered in the Section 5.5. below.

5.5 Mechanisms responsible for degradation of resin–dentine bonds

5.5.1 Resin degradation – esterases versus water sorption

Most dental resin monomers are esters of methacrylic acid and other derivatives that are used to make the monomers into more hydrophilic monomethacrylates or more hydrophobic dimethacrylates. These ester linkages are theoretically susceptible to a number of esterases in body fluids. The early demonstrations of esterase-induced hydrolysis of methacrylates were reported by Freund and Munksgaard (1990) and Munksgaard and Freund (1990) using liver esterases. Several years later, Bean *et al.* (1994) showed that microsomal enzymes could also attack methacrylates. The most sophisticated study compared the activity of acetylcholinesterase, cholesterol esterase, porcine liver esterase and pancreatic lipase on a wide variety of polymers and measured their maximum velocity of esterase activity ($V_{\max}$) and the concentration of the substrate that gives half the maximal velocity (K_m) (Yourtee *et al.*, 2001). Those authors showed that aromatic methacrylate derivatives were more resistant to enzyme attack than aliphatic derivatives.

Others have shown that cholesterol esterase can attack poly(ester) urea-urethanes (Wang *et al.*, 1997) and resin composites (Santerre *et al.*, 1999, 2001). Indeed, more recent work has shown that saliva contains sufficient esterase activity to attack resin composites (Liu *et al.*, 2005).

This enzyme activity can certainly soften exposed resin composite surfaces and may facilitate wear by causing loss of filler particles (Söderholm *et al.*, 1984). Whether there are similar esterases in dentinal fluid remains to be determined. How they might reach resin–dentine interfaces is also unclear. One would expect that resin tags would seal dentinal tubules and prevent percolation of dentinal fluid into hybrid layers. However, recent reports of the high permeability of single-bottle and self-etching adhesives (see Section 5.3 above) indicates that this assumption needs to be tested.

Clearly, resin–dentine bond strengths tend to fall over time (see Koshiro *et al.*, 2004; Shirai *et al.*, 2005). Electron microscopy of the failed bonds

reveals a loss of resin from around the collagen fibrils of the hybrid layer. How much the fall in bond strength is due to degradation of resin properties vs. loss of collagen fibrils (see below) remains to be determined.

The loss of resin could be due to leaching of unpolymerized monomers or oligomers and their replacement with water. Recent water sorption/solubility studies of contemporary dental adhesives (Ito *et al.*, 2005b; Malacarne *et al.*, 2006; Yiu *et al.*, 2006b) indicate that the hydrophilic adhesives in common use have much higher water sorptions than the more hydrophobic solvent-free BisGMA/TEGDMA resins used to seal three-step adhesives. This water uptake swells and plasticizes the polymers, lowering their stiffness (Ito *et al.*, 2005b), making them more compliant and lowering their resin–dentine bond strengths (Carrilho *et al.*, 2004; Yiu *et al.*, 2004). We believe that the influence of water sorption is underappreciated (Carrilho *et al.*, 2005a). The Ito *et al.* (2005b) study also compared reductions in hydrophilic vs. hydrophobic resins in water vs. hexadecane, a pure oil that is too large to plasticize resins. Specimens stored in hexadecane showed no significant decrease in stiffness over the 3-day experiment. For etch-and-rinse adhesives, the use of ethanol-wet bonding permits infiltration of hydrophobic resins into dentine. These resins absorb little water and may maintain their mechanical properties much longer than hydrophilic resins. This technique has not yet been clinically evaluated.

5.5.2 Collagen degradation – matrix metalloproteinases

The first *in vivo* study of the degradation of resin–dentine bonds in humans was performed by Hashimoto *et al.* (2000, 2001). They prepared cavities in the primary molars of children as part of their regular dental care. They bonded resin composites to the cavities using Scotchbond Multi-Purpose (3M) on acid-etched enamel and dentine. After 1–3 years, when the teeth were ready to exfoliate, they recovered the teeth and measured microtensile bond strength as well as examining the bonds by SEM. They reported 47% reductions in microtensile bond strength in 1 year and 68% reductions after 2–3 years. This was associated with a loss of resin and collagen fibrils from the hybrid layer. They interpreted their results as being due to ‘hydrolysis’ of collagen, but did not specify any mechanism.

Several long-term *in vitro* TEM studies of resin–dentine bonds reported a loss of staining and a loss of cross-banded collagen from the hybrid layers after 4–5 years (De Munck *et al.*, 2003; Armstrong *et al.*, 2004; Garcia-Godoy *et al.*, 2007). The degradation was patchy and non-uniform but was extensive. The high resolution provided by TEM examination suggested that collagen had been converted to gelatin. That is, the hybrid layer was not empty but contained organic material that did not take up heavy metal stains which are typically taken up by native cross-banded collagen fibrils.

We believed that the loss of collagen was due to the action of endogenous collagenases (MMPs) in the dentine matrix. Several studies reported the presence of MMP-2 (gelatinases A) in dentine (Martin-De Las Heras *et al.*, 2000), or confirmed the presence of MMP-2 in dentine and reported the presence of MMP-9 (gelatinase B) in dentine (Mazzoni *et al.*, 2007). Recently, the presence of MMP-8, a true collagenase, has also been reported in dentine (Sulkala *et al.*, 2007) along with MMP-2 and -9, all in their activated forms.

To demonstrate the degradation of dentine matrices by endogenous MMPs, we simply acid-etched disks of dentine with 37% phosphoric acid for 15 s and then placed them in buffered calcium- and phosphate-containing media with or without four protease inhibitors that are used in biochemistry to inhibit MMPs during collagen extraction and purification (Pashley *et al.*, 2004). Half the etched specimens were incubated in buffer while the other half were incubated in mineral oil. Specimens were removed and processed for TEM observation of the quality of the collagen after 24 h, 90 days and 250 days. After 90 days of incubation in the absence of protease inhibitors, the naked collagen fibrils began thinning on the ends and swelling in the center. By 250 days, the collagen had degraded down to the mineralized base. In specimens incubated in the presence of protease inhibitors, the collagen fibrils appeared normal. Similarly, specimens incubated in oil looked normal over the 250 days. MMPs are, technically, hydrolases. That is, they catalyze the addition of water across specific peptide bonds. In the absence of water, that is, in specimens immersed in oil, MMPs cannot cleave collagen. In that same study, we incubated mineralized dentine powder with fluorescein-labeled soluble collagen to determine if dentine powder could split soluble collagen into fluorescent fragments. This functional assay measured low but detectable collagenase activity that was inhibited 73% by the protease inhibitors, and almost 100% by 0.2% chlorhexidine digluconate, a known inhibitor of MMP-2, -8 and -9 (Gendron *et al.*, 1999).

Acid-etching with 37% phosphoric acid (15 s) produced a large (i.e. 65%) decrease in the collagenolytic activity of dentine (Pashley *et al.*, 2004). Since the pH of those liquids or gels was between 0.1 and 0.4, it was thought that the phosphoric acid denatured the enzyme(s) as rapidly as they were uncovered by demineralization. That observation was initially thought to be therapeutically helpful. That is, if during bonding, etching dentine with phosphoric acid denatured the MMPs bound to collagen, but did not denature collagen itself, then the subsequently created hybrid layers would remain stable over time. Arguing against that idea were the TEM studies (De Munck *et al.*, 2003; Armstrong *et al.*, 2004; Garcia-Godoy *et al.*, 2007) that showed large regions of destruction of etch-and-rinse hybrid layers, presumably by MMP collagenases, in the absence of bacteria. The confusion was cleared up when Mazzoni *et al.* (2006) reported that although

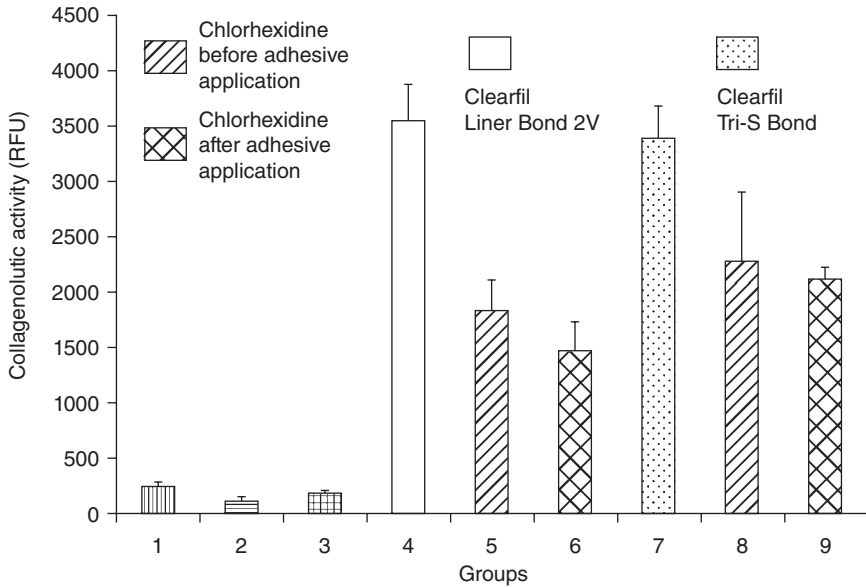
phosphoric acid-etching did lower the collagenolytic activity of the dentine matrix, subsequently applied adhesive agents (Single Bond, One Step, Excite, Prime & Bond or Optibond Solo) were acidic enough (i.e. pHs between 2.6 and 4.7) to expose and activate new MMPs. The pH of these adhesives was sufficient to demineralize dentine without denaturing the collagenases. The gelatinolytic activity of dentine powder was highest for the etch-and-rinse adhesives with the lowest pH (Prime & Bond pH 2.6, Optibond Solo pH 2.7) and lowest for One-Step which had the highest pH (pH 4.6). One of the major MMPs in dentine is MMP-2 (Martin De Las Heras *et al.*, 2000; Mazzoni *et al.*, 2006; Sulkaka *et al.*, 2007). Although classified as a gelatinase, MMP-2 is also an effective collagenase (Aimes and Quigley, 1995).

5.5.3 Effects of acids on dentine MMPs

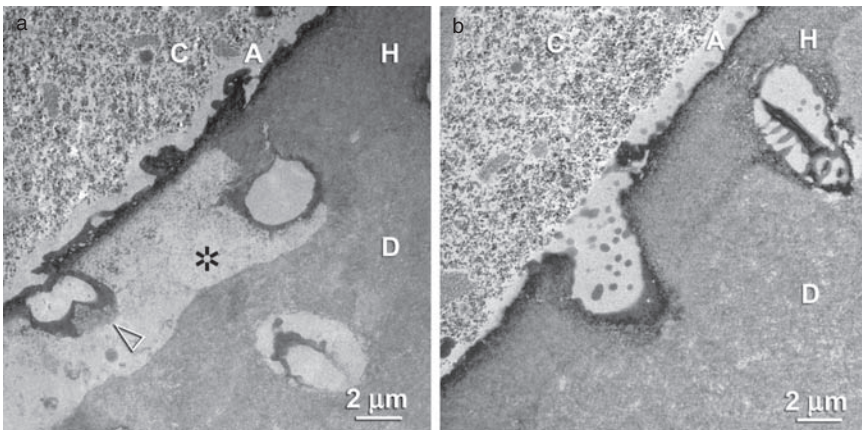
Although the exposure of MMPs to acidic pH (*c.* pH 4.5) had been known to activate MMPs in carious dentine (Tjäderhane *et al.*, 1998), no one had thought that self-etching dentine adhesives with pH values between 1.5 and 2.7 would uncover or activate the MMPs in normal dentine. This was recently demonstrated (Nishitani *et al.*, 2006a) when normal mineralized human dentine powder was mixed with Clearfil Tri-S Bond, G-Bond or Adper Prompt L-Pop for 20s to 5 min. The etching was terminated by extracting the adhesives from the powder with acetone. Functional enzyme activity was evaluated with fluorescein-labeled gelatin or collagen. All self-etching adhesives increased the gelatinolytic and collagenolytic activity of dentine powder more than 10-fold, but this activity could be almost completely inhibited with 0.2% chlorhexidine (CHX).

Similar increases in the collagenolytic activity of root canal dentine (Fig. 5.17) were reported following application of self-etching primers (Clearfil Liner Bond 2V or Clearfil Tri-S Bond, Kuraray Medical Inc.) to dentine shavings that came out of root canals during rotary filing and shaping with Gates–Glidden burs (Tay *et al.*, 2006).

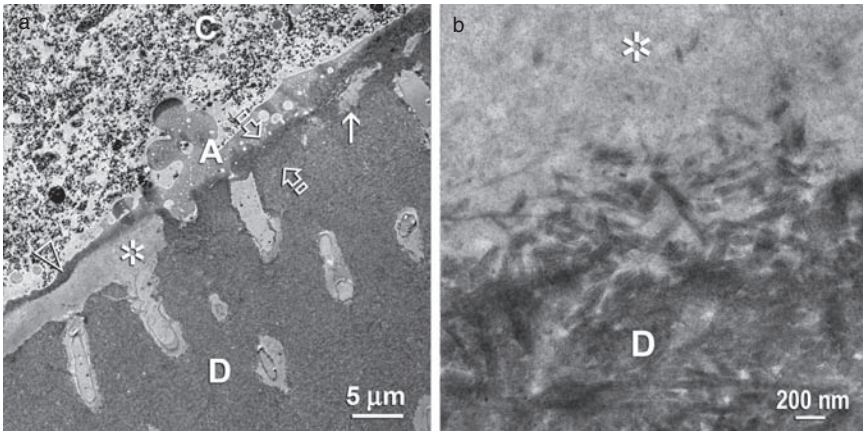
Although *in vitro* studies are useful, is there any *in vivo* evidence of degeneration of hybrid layers? In a recent study by Hebling *et al.* (2005), carious primary molars were treated by restoring class I cavity preparations with Single Bond. In a split-mouth design, teeth on one side were treated with 2% CHX just after acid-etching, before bonding (experimental group) or had no CHX treatment (control group). After 6 months, the exfoliating teeth were extracted and processed for TEM. Control hybrid layers revealed extensive loss of cross-banded collagen with the creation of voids in the hybrid layer (Fig. 5.18a), while the CHX-treated experimental teeth were shown to have normal hybrid layers (Fig. 5.18b) without any signs of degradation. These TEM observations were recently confirmed in normal



5.17 Bar graph showing the collagenolytic activity of dentine chips from root canals after various treatments. Bars 1 to 3 are the background fluorescence of dentine chips before adding fluorescent collagen.



5.18 Transmission electron micrographs of resin-bonded primary caries-affected dentine after 6 months of function: *a* control bonding loss of hybrid layer substance (asterisk) with remnant resin tags (open arrowhead); *b* after pretreatment of acid-etched dentine with 2% chlorhexidine digluconate for 30 s, showing the preservation of hybrid layers (Hebling *et al.*, 2005). (C, composite; H, hybrid layer; A, adhesive; D, dentine.)



5.19 Transmission electron micrographs of resin-bonded normal dentine after 14 months in function: *a* a low magnification view showing a zone of more complete degradation (asterisk) and zones of partial degradation of the collagen matrix (arrow) within the hybrid layer (between open arrows). In the zone of more complete degradation, only the surface of the hybrid layer remained (open arrowhead); *b* a high-magnification view of the region indicated by the asterisk in *a*. The collagen fibrils within the original hybrid layer have completely degraded into microfibrils (not shown) and further into a stainable, amorphous material (asterisk) which probably consisted of peptides and amino acids. (C, composite; A, adhesive; D, dentine.)

permanent dentine in function for 14 months *in vivo* (Fig. 19a and b; Carrilho *et al.*, 2007). The control teeth bonded with Single Bond showed degradation of the hybrid layer while the experimental teeth treated with 2% CHX before bonding with Single Bond did not show any signs of degradation.

What is the evidence that degenerative changes in the hybrid layer produce lower bond strengths? In the De Munck *et al.* (2003) study that showed extensive loss of cross-banded collagen in hybrid layers over four years *in vitro*, OptiBond-, Single Bond- and Scotchbond Multi-Purpose-restored teeth showed microtensile bond strengths of 53.6 ± 8.2 , 52.2 ± 9.1 and 45.6 ± 11.1 MPa, respectively, after 24 h. After four years of direct *in vitro* water storage, the bond strength of Single Bond fell significantly ($p < 0.05$) to about 22 MPa, while that of Scotchbond Multi-Purpose fell to 32 MPa ($p = 0.069$); however, OptiBond FL bonds did not decrease in strength. In the Armstrong *et al.* (2004) study, the bond strength of OptiBond FL fell significantly ($p < 0.001$) from 46.7 to 17.7 MPa over five years of *in vitro* storage. In a one-year *in vitro* study, microtensile dentine bond strengths fell 53–71% (Carrilho *et al.*, 2005b).

In an *in vivo* monkey study, Koshiro *et al.* (2004), reported that Single Bond-restored class V resin composites showed significantly lower bond strengths (48.1 ± 7.4 vs. 11.7 ± 9.3 MPa) when one-day bonds were compared with one-year bonds. Similarly, Unifil Bond, a self-etching primer adhesive system, showed a fall in bond strength from 38.7 ± 9.0 to 14.4 ± 9.3 MPa in one year. When the failed bonds were examined by high-resolution SEM, the Unifil Bond specimens exhibited an increase in the porosity of the hybrid layers, while the hybrid layers in the Single Bond group showed fewer than normal collagen fibrils and a loss of resin in the hybrid layer.

An even more convincing *in vivo* study has been reported (Carrilho *et al.*, 2007). This clinical study was done on normal erupted human third molars in a split-mouth design. Control teeth received class I cavity preparations that were restored with Single Bond and resin composite. Experimental teeth on the opposite side of the mouth were treated with 2% CHX immediately after etching but before bonding with Single Bond. Three pairs of teeth were extracted immediately to permit comparison of the microtensile bond strength of Single Bond $\pm$ CHX and to reveal their TEM ultrastructure. Nine additional pairs of teeth were extracted 14 months later. In the control group, the bond strengths had fallen from 29.3 ± 9.0 to 19.0 ± 5.2 MPa. The experimental CHX-treated teeth showed one-day bond strengths of 32.7 ± 7.6 MPa, while the 14 month values were 32.2 ± 7.2 MPa. That is, there was no significant loss of bond strength in the CHX-treated specimens. TEM examination of the control hybrid layers after 14 months showed extensive loss of cross-linked collagen and large voids within the hybrid layer, while the hybrid layers in the CHX-treated controls looked the same as the one-day control or experimental specimens.

This body of accumulating evidence strongly suggests that endogenous MMPs are uncovered and/or activated by many, if not all, dentine bonding procedures. The collagen fibrils of the hybrid layer by being anchored into the underlying mineralized matrix, provide micromechanical retention of adhesive resins that, in turn, retain resin composites. The only continuity between adhesively retained restorations and the hybrid layer are resin tags in the tubules, and nanometer-wide adhesive resin extensions that pass around and between collagen fibrils. When normal hybrid layers receive tensile stressing, we speculate that the collagen fibrils share the stress with this resin network by being loaded in parallel. If, however, endogenous collagenases/gelatinases are activated during dentine bonding procedures, resulting in cleavage of collagen and its conversion to weaker gelatin (i.e. loss of cross-banded collagen), then stresses applied to this weakened hybrid layer will be borne by the stiffest surviving material. If that is resin, the resin meshwork may pull out of the ‘gelatinized’ hybrid layer, producing lower bond strengths (Tay *et al.*, 2000).

5.5.4 Possible solutions to the loss of mechanical stability of resin–dentine bonds

Clearly, the durability of resin–dentine bonds is much more complicated than was previously thought. However, so much has been learned over the past decade, that we believe that major advances can be achieved to make these bonds much more durable. Obviously, one approach to more stable resin–dentine bonds is the use of 2% CHX or other MMP inhibitors applied to the dentine matrix in etch-and-rinse adhesives. However, when we pretreated mineralized dentine powder with various concentrations of CHX before bonding with self-etching adhesives to inhibit the MMPs in dentine, the inhibiting effect of CHX was lost because the self-etching acidic adhesives stripped the CHX from the mineralized matrix during acid-etching (Y. Nishitani, unpublished observations, 2006). When we added CHX to the self-etching adhesives and then applied the mixture to mineralized dentine, we were unable to inhibit MMPs. Presumably, CHX cannot bind to the dentine matrix in the presence of an acidic environment. It may be possible to find MMP inhibitors that can remain bound to the matrix in an acidic environment.

5.6 Summary

Studies on the stability of resin–dentine bonds have implicated instability in both resins and the dentine matrix. The notion that one can create perfect resin coatings on wet dentine, *in situ*, at 37°C, using solvated comonomers that are light-cured for less than 1 min, would be regarded by non-dental polymer chemists as absurd. That we are partially successful is a tribute to both dental manufacturers and clinician's skills. Non-dental experts in collagenous extracellular matrices are surprised to discover that dentists have only recently considered the clinical implications of trying to encapsulate endogenous collagenase enzymes bound to collagen fibrils with resin, without any attempts to inhibit their activity.

Resin–dentine bonding is a unique form of tissue engineering in that we utilize the natural collagen fibril matrix of demineralized dentine, which is continuous with the underlying mineralized matrix, as our scaffold for resin infiltration. Unlike conventional engineering tissues that are expected to degrade within weeks to months, dentists want the matrix to last for decades. This may be possible if we focus more research on how to stabilize dentine matrices and how to improve both the comonomers that we use and the solvents employed in resin–dentine bonding.

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Dental cements: formulations and handling techniques

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6.1 Introduction

Cements are used in dental practice primarily for retaining or sealing restorations and prosthetic devices in a fixed position within the mouth. These cements are often referred to as 'luting cements'. Although cement materials are also used for a variety of special-purpose applications in dentistry – e.g. cavity lining, direct restorations, and orthodontic, periodontic and surgical procedures – the scope of this chapter is limited to dental luting cements. The word 'luting' implies the use of a molded or moldable article to seal a space or to cement two components together. Traditionally, cements are formed by an acid–base reaction in which an acidic component (typically a liquid) is mixed with a basic component (typically a powder). The search for better materials has inspired many chemical developments to meet the ever-changing needs of the dental practitioner and, coupled with innovations in delivery devices, has made the cementation procedures faster, easier and more predictable. Functionally these cements must withstand masticatory stresses and maintain their integrity in the oral environment while transferring the stresses from the fixed prosthodontic device, e.g. crowns, bridges, etc., to the tooth structure. A wide range of materials with differing properties are available for final luting of crowns, bridges, inlays, onlays, posts and pin restorations. This chapter addresses the six major classes of cements used today: zinc phosphate, zinc polycarboxylate, conventional glass-ionomer, resin-modified glass-ionomer (RMGI), traditional resin and self-adhesive resin cements.

6.1.1 General requirements of dental cements

An ideal luting cement should have physicommechanical properties resembling those of dentine. However, the cements available today have a wide range of properties depending on their composition and hence are restricted in their use to specific indications (Donovan and Cho, 1999). Table 6.1

Table 6.1 Luting cement comparison

Cement type	Areas of application	Strengths	Weaknesses
Zinc phosphate	Routine applications in metal-supported crowns and bridges	Over 100 years of clinical experience	Occasional post-operative sensitivity Low hardness High solubility
Polycarboxylate	Retention of metal-supported crowns and bridges Long-term provisional crowns	30+ years of clinical experience Molecular bonding to tooth surface Low post-operative sensitivity	High solubility and erosion Low hardness
Conventional glass ionomer	Routine application of metal-supported crowns and bridges	25+ years of clinical experience Fluoride ion release Molecular bonding to tooth structure Medium strength Simplicity of use	Occasional post-operative sensitivity Sensitive to water and mechanical loading Solubility and erosion
Resin-modified glass ionomer	Routine application of metal-supported crowns and bridges Limited application for high-strength ceramics	15+ years of clinical experience Minimal post-operative sensitivity Fluoride ion release Molecular bonding to tooth structure Medium strength Simplicity of use	Not suitable for low-strength ceramics due to expansion
Resin cements (composites)	Metal-supported restoration Most all ceramic crowns	10–20 years of clinical experience High adhesion when used with adhesives High mechanical properties Low solubility Good aesthetics	Difficult to use Requires use of separate adhesive and etching Potential for post-operative sensitivity Difficult to clean-up Technique sensitive No or little fluoride release
Self-adhesive resin cement	All metal-based, ceramic and indirect composite restorations with the exception of veneers	Convenient, easy technique Most require no additional priming High mechanical properties Low solubility Good esthetics Easy clean-up	Limited clinical history Low to no fluoride release

Table 6.2 Specifications requirements for dental cements

	Zinc phosphate ¹	Zinc polycarboxylate ¹	Conventional glass ionomers ¹	Resin luting cements ²
Setting time (min)				
Minimum	2.5	2.5	2.5	
Maximum	8.0	8.0	8.0	10
Film thickness (m)	25	25	25	50
Lactic acid erosion (m/h), maximum	2.0	2.0	0.05	—

¹ Covered by ISO 9917-1 for dental water-based cements.

² Covered by ISO 4049 polymer-based dental materials.

outlines the current material classes of luting cements, their areas of applications, advantages and weaknesses. The properties usually tested for a cement are its setting time, film thickness, compressive strength, diametral tensile strength, modulus of elasticity, fracture toughness, bond strength to dentine (for adhesive luting cements), acid erosion and solubility. Several international standards define the procedure for measuring the properties and minimum acceptable levels (Table 6.2). When selecting cements it is important to look for a balance of properties rather than focus on any particular characteristic. Thus, although high compressive strength, together with good rigidity, is important to resist forces due to mastication, too high a modulus may be the cause of brittleness of the cement. An overall good combination of viscoelastic properties will ensure that the cement can absorb stresses due to chewing. Retention of the crown also depends heavily on its fit and the geometry of the core preparation. Hence properties such as film thickness of the cement, minimal solubility and erosion, and its adhesive properties are also of paramount importance. The strength of the crown or bridge material itself is also a determining factor in the choice of the cement. An adequate marginal seal is essential to reduce plaque accumulation, periodontal disease and recurrent caries. The availability of high levels of sustained fluoride release on a prolonged basis from certain cements is beneficial since this feature is thought to reduce the risk of recurrent caries.

Luting cements are generally classified according to their chemical composition. Although the acid–base nature has been preserved in many of the modern materials the resin-based luting cements differ significantly in the cement-forming reaction. The cements are usually supplied as two-part systems that have to be mixed just before use and achieve some sort of chemical reaction in the oral environment to achieve setting. Historically,

these have been available as a powder–liquid formulation with only the most recent advances as two-paste systems supplied in convenient delivery devices. In addition to all the important physicochemical properties of a luting cement perhaps the most important characteristic that determines its long-term clinical success is its ease of handling and manipulation during the clinical procedure. Hence handling and manipulative characteristics such as its delivery system, mixing properties, working time, ease of clean-up and setting characteristics often become the determining factors for the clinician in choosing the cement for a particular application.

6.2 Zinc phosphate cements

Zinc phosphate cement has been a mainstay in dentistry for crown and bridge applications for well over a century and has undergone many refinements in formulation and compounding. However, with the advent of newer chemical technologies its use has gradually declined over the last decade. This type of cement is supplied as a powder–liquid formulation.

6.2.1 Composition

The powder consists of mainly amorphous zinc oxide as the major ingredient with small amounts of oxides of magnesium and bismuth added mainly to facilitate the calcining process for manufacture of the powder. Small quantities of silica (typically fumed) are often added to aid in providing the right viscosity and yield stress. Minor amounts of barium and calcium compounds may be added by various manufacturers to provide a smooth, creamy mix, which is desirable for easy flow during cementation of the restoration. Some products also contain tannin fluoride although it is doubtful if the amount of fluoride released is of clinical significance.

The liquid consists of an aqueous mixture of orthophosphoric acid with small amounts of aluminum and zinc phosphates which act as buffers in reducing the reactivity of the free acid. The amount of water used in the formulation is quite critical since it dictates the setting time – too little prolongs the setting time whereas too much shortens it.

6.2.2 Mechanism of action

Setting reaction

When the alkaline zinc oxide powder is incorporated in the acidic liquid an exothermic acid–base reaction ensues. Initially, the mix becomes fluid and creamy which aids in the placement of the prosthodontic device. Within a

few minutes the mass hardens to a set cement which may contain varying amounts of crystalline phosphates of zinc including the formation of hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, in the presence of excess moisture.

6.2.3 Manipulation

The proper proportioning of the powder and liquid components and the mixing technique are critical to ensuring adequate clinical success with these materials. The proper amount of powder should be slowly incorporated in incremental amounts into the liquid on a cool slab (at approximately 21 °C) since the mixing temperature has a profound influence on the setting characteristics. Aggressive mixing results in too high an exotherm for this class of technique-sensitive material. Spreading the mix over a large area on the cool glass slab helps to dissipate the heat. The liquid is rather hygroscopic, absorbing water if exposed to excessive humidity, and losing water if kept in a dry atmosphere or if the vial is not kept properly sealed.

6.2.4 Properties

The clinically significant properties of zinc phosphate cements include setting time, solubility and film thickness. The mechanical properties of importance are strength, modulus of elasticity and hardness. Most commercial materials meet the American National Standards Institute/American Dental Association (ANSI/ADA) Specification 96 (ISO 9917-1: 2003). Illustrative ranges are provided in Table 6.3. In comparison with the more recent types of cements, the modulus of elasticity is quite high, which causes them to be rather brittle materials that are prone to fracture. The solubility of the set cement is relatively high at about 0.2% in 24h compared with some other classes of cements. Furthermore, these materials have virtually no adhesion to the dentinal core of the tooth preparation.

6.2.5 Clinical usage

Zinc phosphate cements have had a long history of clinical usage for routine luting of metal-supported crowns and bridges (Donovan and Cho, 1999). Other uses include cementation of orthodontic bands, as a basing material and as temporary restorations. Occasional post-operative sensitivity has been reported by patients with the use of this type of cement (Johnson *et al.*, 1993). The exact cause of this is not known and has been linked to acidity of the un-neutralized orthophosphoric acid residues in the cement and/or the movement of dentinal fluid across the tubules in

Table 6.3 Typical properties of luting cements

	Zinc phosphate	Zinc polycarboxylate	Conventional glass ionomer	Resin-modified glass ionomer	Resin luting cements
Compressive strength (MPa)	95–130	55–85	90–170	85–150	180–250
Tensile strength (MPa)	3.0–4.5	10–15	10–24	15–25	30–40
Elastic modulus (GPa)	9.3–13.4	4.4–5.0	3.5–6.4	2.5–6.0	4.0–11.0
Bond Strength to dentine (MPa)	0	2–6	2–6	2–10	18–30
Fracture toughness (MN/m ^{3/2})	0	0.38	0.33–0.35	0.78	0.75–1.2
Solubility in water (%) in 24 h)	<0.20	<0.05	0.4–1.5	0.0–0.05	0.0–0.13

Adapted from: Craig (1997); Li and White (1999); RelyX™ Luting Cement and Luting Plus Cement Technical product profile (3M-ESPE, 2004).

excessively desiccated dentine due to an improper seal. The use of resin desensitizing agents has been advocated to counter post-operative sensitivity without compromising crown retention (Swift *et al.*, 1997; Johnson *et al.*, 2004).

6.3 Zinc polycarboxylate cements

Zinc polycarboxylate cements, sometimes referred to simply as ‘polycarboxylate’ or ‘polyacrylate’ cements, are based on the reaction of zinc oxide with polycarboxylic (same as polyalkenoic) acid in water (Smith, 1968). Like the zinc phosphate cements these are also supplied as powder–liquid compositions.

6.3.1 Composition

The powder is quite similar to that of zinc phosphate cements and consists mainly of sintered zinc oxide ground to a fine particle size. The sintering

process reduces the reactivity of the amorphous zinc oxide and helps in the manipulation of the cement. Small amounts of magnesium oxide (1–5%) are added to aid the sintering process while the incorporation of fumed silica helps in the mixing and flow of the cement. Fluoride salts, e.g. stannous fluoride, may also be incorporated in small amounts to improve mechanical strength and to serve as a source of leachable fluoride. In some commercial embodiments the powder is coated with 5–20% of anhydrous polyacrylic acid to make it less technique-sensitive during the mixing process.

The liquid consists of an aqueous solution of a polycarboxylic acid, generally a homopolymer of polyacrylic acid or a copolymer of acrylic acid with itaconic or maleic acids. The average molecular weight (weight average) is usually in the range 20000–50000. The viscosity of the solution may be controlled by the addition of small amounts of tartaric acid. For products where the powder is coated with polycarboxylic acid, the liquid is either a dilute solution of the polyacid or simply water.

6.3.2 Mechanism of action

Setting reaction

The polycarboxylic acid reacts with the basic zinc oxide in a neutralization reaction forming a zinc polycarboxylate complex salt (Smith, 1983). This results in the formation of a cross-linked polycarboxylate hydrogel reinforced by the oxide particles. The cross-linked gel is bound to the polyanion chains by electrostatic interaction. The setting reaction has been studied by infrared spectroscopy which shows that the carboxylic acid groups (COOH) are progressively converted to carboxylate (COO⁻) groups as the cement hardens.

Water plays several important roles in controlling the chemistry and properties of all acid–base cements. These are outlined below.

- 1 As a diffusion medium. Water is needed for the acids to ionize so that the protons can be dissociated and solvated and the acidic property can be manifested. It is also needed for the diffusion of the metallic ions of the bases (e.g. zinc oxide) so that these can enter the liquid phases and thus react with the acid. In addition, it is essential for the diffusion of fluoride ions, where present, out of the set cement.
- 2 As a stabilizer of the carboxylate complexes. A portion of the water coordinates with the zinc carboxylate complexes by electron donation to stabilize them. This is known as bound water and cannot be easily removed from the stabilized matrix.

- 3 As a plasticizer. The residual water helps to plasticize the set cement and makes it more resilient and less prone to failure by fracture.

6.3.3 Manipulation

The vast majority of the commercial polycarboxylate cements are supplied with a bottle of powder, a measuring scoop and a vial dispenser containing the liquid. In one product (Durelon™, 3M ESPE) the liquid is provided in a calibrated dispenser. It is recommended to dispense the liquid on a non-absorptive surface, e.g. glass or a waxed paper mixing pad so as to avoid loss of water and thickening of the liquid. The correct proportions of powder and liquid are generally hand-spatulated with a metal mixing spatula for a specified time (usually 30–45 s). The time from the start of mix to the end of manipulation is referred to as the ‘working time’, which is dependent on the ambient temperature, decreasing at higher temperatures. Although typical working times at 23 °C are 2–4 min, a longer window may not necessarily be advantageous since it also translates to a longer set time in the mouth (hence longer chair time). As with zinc phosphate cements, using a cooled glass slab extends the working time. The mix should be creamy and should be placed while it is still glossy and before the onset of the elastomeric phase, commonly referred to as ‘cobwebbing’. If the mix loses its gloss before placement, it should be discarded since adhesion will be compromised. At least one product is supplied in a predosed capsule format, which has to be activated and triturated before to placement. The mixed cement is viscous yet thixotropic, i.e. it flows better under increasing pressure. Any excess cement should be removed before it reaches a rubbery consistency.

6.3.4 Properties

Setting and working time

Setting and working time are two important clinically relevant parameters for any cement. The working time is the time available for the manipulation of the unset cement while the setting time is the time required by the material to set or harden from a fluid or plastic state to a rigid one. While at the end of the setting time the hardening reaction may not be complete it generally progresses far enough for the dentist to proceed to successive steps in the procedure without fear of premature dislodgement of the prosthesis. There is no standard value for the working time, but it should be reasonably long so that adequate time is available for mixing and placing the cement. Since both the working time and setting time are dependent on the same chemical reaction the former should not be too long to ensure the setting of the cement within a reasonable time. The minimum and maximum

requirements of setting time are specified by the ISO 9917-1 specification for water-based cements as outlined in Table 6.2. The rate of setting is affected by the following parameters:

- reactivity of the zinc oxide;
- particle size of the zinc oxide;
- presence of additives;
- molecular weight and concentration of the polyacrylic acid;
- powder/liquid ratio.

The first four parameters are controlled by the manufacturer. The last one is dependent on the operator. Hence, accurate dispensing of the powder and liquid are essential if consistent setting is to be obtained. For commercial cements the working times are 2–4 min and set times are between 5 and 8 min.

Strength

Table 6.3 shows typical values of properties of this class of cement compared with other luting cements. In general, zinc polycarboxylate cements are lower in compressive strength than zinc phosphates but, due to the presence of a polymeric matrix, are tougher and less brittle. Plastic deformation is exhibited at higher load values, which contributes to the increased toughness of these cements. Compressive and diametral tensile strengths of the cement develop rapidly within the first hour to about 60–80% of its strength at maturity, while it takes about 24 h for maximum strength to be attained.

Solubility and erosion

The solubility of the cements when tested in water alone is low (0.1–0.5%) compared with the zinc phosphate cements, although solubility in distilled water does not always correlate to solubility in oral conditions. These cements are rather susceptible to erosion in an acidic environment, however. A quantitative measure of this property is defined in the ISO 9917-1 specification using the impinging lactic acid jet method devised by Beech and Bandyopadhyay (1983).

Film thickness

These cements appear to be more viscous than other cements but due to their marked thixotropic nature flow well under seating pressure of a prosthetic device to yield acceptable film thickness as defined by specifications (Table 6.2).

Adhesion to tooth structure

Polycarboxylate cements can bond to enamel and dentine by ionic bond formation with the calcium ions of the hydroxyapatite mineral. In order to achieve this it is essential to have the prepared tooth surface free of debris and contaminants. Bond strength values as measured in the laboratory are dependent on the cohesive strength of the cement, particularly its modulus. Measured values are therefore low (enamel 3–13 MPa; dentine 2–4 MPa) compared with RMGIs and resin cements. However, it is debatable whether *in vitro* bond strength measurements are a true reflection of clinical performance. In actual usage, the service life of prostheses cemented with polycarboxylates is quite acceptable clinically.

6.3.5 Clinical usage

Zinc polycarboxylate cements have a fairly long record of clinical success when used for specified indications. The most frequent use is for cementation of cast alloy- and metal-supported inlays, onlays and single-unit crowns. Because of the lower values of compressive modulus these materials should not be used for permanent cementation of long-span bridges. Less frequently they are also used as cavity liners and orthodontic band cementation but in such cases a higher powder/liquid ratio is recommended by manufacturers. The comparatively high long-term solubility and low hardness limit the utility of this class of materials for permanent cementation, resulting in a decline in their use in recent times.

6.4 Conventional glass-ionomer cements

As with other dental materials, the chemistry of dental cements has undergone continual evolution. The conventional glass-ionomer cements combine the technologies and chemistries from silicate and zinc polycarboxylate cements in order to incorporate the desirable characteristics of both. Thus they contain the ion-leachable fluoroaluminosilicate (FAS) glass of silicate cements but avoid their susceptibility to dissolution by substituting the phosphoric acid and its salts with the polymeric carboxylic acids of the zinc polycarboxylate cements (Wilson and Kent, 1971). Like their predecessors, the zinc polycarboxylates, these materials are primarily acid–base cements.

6.4.1 Composition

Although the original systems developed by Wilson and Kent (1971) have undergone several modifications, the essential components of this class of

materials are unchanged and consist of polycarboxylic acid, FAS glass, water and tartaric acid. The polymeric components of most commercial embodiments are copolymers of acrylic acid with itaconic or maleic acid. Tartaric acid is added to the liquid to control the viscosity as well as the working and setting properties of the cement. The basic component is an acid-reactive FAS glass containing additional multivalent ions such as calcium, strontium and lanthanum, some of which are added to provide radiopacity to the set cement. The molar ratio of aluminum to silicon in the glass network has to be carefully controlled (usually 2:3 to 1:1) to provide the right balance of reactivity versus stability. These cements are supplied as bulk powder–liquid formulations as described for the zinc polycarboxylates. Both hydrous and anhydrous forms are available, depending upon the manufacturer. In the latter, the freeze-dried polyacid is mixed with the powder and water is supplied as the liquid. In order to make it convenient for the dentist, manufacturers have developed unit-dose capsules, which are activated just before use by breaking a seal that allows the powder and liquid to come into contact. An amalgam triturator is then used to mix the components mechanically while specially designed delivery guns are provided to extrude the mixed paste directly into the oral cavity. The glass-ionomer luting cements contain a lower powder/liquid ratio, and hence are less viscous upon mixing than the restorative products. Furthermore, the particle size of the glass has to be quite small in order to meet the ISO specifications of film thickness.

6.4.2 Mechanism of action

When the powder and liquid are combined, an acid–base reaction occurs between the FAS glass and the polycarboxylic acid in the presence of water eventually leading to a hardened mass. The actual process of ion extraction from the glass and the resultant complexation reaction are quite elaborate (Billington *et al.*, 2006); however, the essential steps can be described as follows. In the presence of water, the carboxylic acid (COOH) group of the polyacid undergoes partial ionization to yield a carboxylate anion (COO[−]) and a hydrated proton, H₃O⁺. The hydrated proton attacks the surface of the glass particles releasing ions such as calcium, strontium and aluminum ions. The carboxylate ions from the polymer react with these metallic ions to form a salt bridge, resulting in gelation and setting. During the initial setting, non-network bivalent calcium or strontium ions are more rapidly bound to the polyacrylate chains whereas binding to the aluminum ions occurs at later stages. The strength of the cement builds up with time. Silicic acid is initially formed when the glass breaks down, but rapidly polymerizes to form silica hydrogel. As with the zinc carboxylate cements, water plays several important roles in the overall setting of glass-ionomer cements.

A very important by-product of the setting reaction is the release of fluoride ions from the glass matrix. This fluoride release process is sustained and occurs over a long period of time. It is important to realize that this fluoride ion release is a result of the setting reaction and the ion-exchange process in the cement. In this process, the fluoride from the glass is replaced by carboxylate groups and water. Hence, if properly formulated, there is little chance of the cement losing its strength with time. Considerable research has proved that no loss of strength of the glass-ionomer cement occurs over extended storage in water (Mount, 1986).

Role of tartaric acid

Tartaric acid is added to prolong the working time of the cement mix, improve the manipulative characteristics and narrow the range of the setting time. In the absence of this component, the mix becomes rubbery within a few seconds and is rather difficult to work with. The mechanism by which tartaric acid operates is believed to be a temporary suppression of the ionization of the polyacid as well as a preferential extraction of the cations from the glass so that polyacrylate complexes cannot form immediately, thus leading to an increased working time. Later, it sharpens the set and accelerates the hardening of the glass-ionomer mix.

6.4.3 Manipulation

Care must be taken when handling this class of materials since they are quite technique-sensitive and errors could lead to a potentially compromised clinical outcome. Manufacturers of these cements recommend that the powder and liquid are dispensed in defined ratios and then mixed rapidly with a spatula within 30–45 s. The general rule is to first incorporate half the amount of the powder into the liquid and then mix in the other half. The stainless steel cement spatula is most often used, although in some practices a plastic spatula is preferred to avoid potential discoloration. As with all powder–liquid formulations care must be taken to dispense the powder and liquid accurately so as to prevent operational variability. The working and set times are dependent on the powder/liquid ratio. The cement should be used immediately after mixing because the working time is only a few minutes at room temperature. If the ambient temperature is high, working time is even further decreased. If a skin forms over the cement, the mix should be discarded – otherwise adhesion will be compromised. The manipulation is easier for encapsulated versions although it is important to follow the manufacturers' recommended speed and times for trituration of the capsules. Conventional glass ionomers are quite susceptible to moisture contamination. After initial set and removal of excess cement, it is often

advisable to coat the cement margins with a sealing agent supplied by the manufacturer.

6.4.4 Properties

Table 6.2 shows the requirements of this class of cements according to ISO 9917-1 specifications while Table 6.3 provides a comparison with the other classes of luting cements covered in this chapter.

Setting and working time

The factors controlling the setting and working times are similar to those described for the polycarboxylate cements except that here the reactivity and the particle size of the FAS glass, rather than zinc oxide, are of relevance.

Physical properties

The conventional glass ionomers are rather brittle materials with high modulus of elasticity, low diametral tensile strength and low fracture toughness. They are susceptible to desiccation and hence must be protected with a varnish or a resin bonding agent during the setting process. Compressive strengths are similar to those of the zinc phosphate cements. Typical values of the physical properties are given in Table 6.3.

Solubility and erosion

The conventional glass ionomers are susceptible to erosion in the oral environment, particularly under acidic conditions. The maximum acid erosion allowable by the lactic acid jet method is 0.05 μm per hour. The solubility of this class of cements is higher than most other types of permanent luting cements.

Fluoride release

Glass-ionomer materials exhibit a sustained release of fluoride over a long period of time. The uptake of the released fluoride ion in human saliva (Rezk-Lega, 1991) and its incorporation into human enamel have been reported (Scoville 1990). Although considerable debate exists about the 'clinical proof' of the benefits of fluoride, occurrence of recurrent caries in the teeth where these cements have been used is reported to be rare. Studies have shown that glass ionomers inhibit demineralization of the surrounding tooth structures *in vitro* (Hicks *et al.*, 1986) and *in situ* (ten

Cate and van Duinen, 1995), and provide protection against recurrent caries under clinical conditions for patients with high caries risk (Tyas, 1991). This can be attributed to the ability of glass-ionomer cements to inhibit demineralization and enhance remineralization through release of fluoride to the adjacent tissue and surrounding fluid. The rate of fluoride release depends on a particular product brand. However, as a general class, glass ionomers release more fluoride than other types of fluoride-releasing materials.

Adhesion

Like the polycarboxylate cements, the conventional glass ionomers can bond to the calcium of hydroxyapatite of tooth tissue. Despite the low *in vitro* bond strength values shown in Table 6.3, the clinical retention of appliances and restorations with this class of materials is remarkably high.

Post-operative sensitivity

In the past, one of the common complaints against conventional glass-ionomer luting cements has been the high incidence of post-operative sensitivity (Wozniak, 1984) with greater incidence reported for the ‘anhydrous’ type (Simmons, 1986). The most frequent reasons cited for post-operative dentinal hypersensitivity are as given below.

- Desiccation of the tooth. The glass ionomers require water for their setting and may absorb water from the dentinal tubules during this process. This phenomenon is thought to be more prevalent in the anhydrous cements where the dried polycarboxylic acid also needs water for rehydration.
- Initial low pH of the material (although it increases rapidly during the setting process) may irritate the pulp.
- Moisture contamination leading to poor sealing of the tooth and improper margins, hence leakage to bacteria and their by-products.
- Too low a viscosity of the mix causing fluid to be forced down the dentinal tubules during seating of the prosthesis.

The lower values of pH (higher acidity) encountered for prolonged periods during setting of conventional glass ionomers compared with other types of cements was cited as a possible reason for pulp sensitivity (Smith and Ruse, 1986). The diffusion of acid was observed through 0.25 mm dentine disks (Hiraishi *et al.*, 2003). However, it has been demonstrated that by following proper clinical procedures during cementation the operator can minimize or eliminate the occurrence of post-operative sensitivity (Pameijer and Nilner, 1994; Kern *et al.*, 1996).

6.4.5 Clinical usage

Although somewhat technique-sensitive, conventional glass-ionomer luting cements have a good clinical history and are employed primarily for the cementation of permanent metal and porcelain-fused-to-metal (PFM) crowns, for cementation of posts and as orthodontic band cement. The prolonged release of fluoride makes them particularly attractive for conditions where the risk of secondary caries is high. According to some manufacturers the use of polyacrylic acid conditioner is contraindicated in crown and bridge procedures so that the smear layer on the abutments remains to act as a protective layer. Their prolonged maturation time, however, allows for early water sensitivity (Curtis *et al.*, 1993) and they are also more susceptible to hydrolytic degradation than the more insoluble RMGIs or composite luting cements. For this reason, it is advisable to use protective agents such as varnishes or resin-glazes along the crown margins (Rodrigues-Garcia *et al.*, 1995; McComb and Nathanson, 1999).

6.5 Resin-modified glass-ionomer cements

RMGIs, developed in the late 1980s (Mitra, 1989), are more recent entrants into the dental cement arena, having been first introduced commercially as a luting cement in 1994. This class of cements is less technique-sensitive than the conventional glass-ionomer materials and possesses some very favorable physicommechanical properties compared with conventional GI materials (Mitra, 1994; Uno *et al.*, 1996) yet releases similar levels of fluoride (Mitra, 1991a, b; Nagamine *et al.*, 1997; Tantbirojn *et al.*, 2005). Since the RMGI luting cements also allow easy removal of excess cement, show minimal post-operative sensitivity and, so far, have exhibited good clinical performance and durability, this class of material has rapidly become one of the most popular materials for routine crown and bridge applications (Christensen, 1995). Improvements in delivery format have now consolidated their use.

6.5.1 Composition

The first-generation materials were supplied as powder–liquid configurations and are available in hand-mix or encapsulated versions. Vast differences do exist between products from different manufacturers; hence care has to be taken in choosing a particular commercial product for clinical use. The essential components of a true RMGI are:

- polycarboxylic acid copolymer often modified with pendant methacrylate groups;

- FAS glass;
- water;
- water-compatible methacrylate monomers;
- free-radical initiators.

Polymeric component

The RMGIs contain some methacrylate components common in resin composites. There are two ways in which the methacrylate component can be introduced. In the first RMGIs introduced to the market, the polycarboxylic acid copolymer chain is modified to contain a pendant methacrylate group. This was achieved by treating some of the carboxylic acid groups of the polycarboxylic acid with isocyanatoethyl methacrylate to provide pendant methacrylate groups connected through the hydrolytically stable amide linkages. The first commercial glass-ionomer material (Vitrebond™ RMGI liner, 3M ESPE) was introduced in 1988 using this type of chemistry. The RMGI luting cements from this manufacturer also use the same chemistry.

In addition to the methacrylate-modified carboxylic acid, the liquid portion contains a water-miscible methacrylate monomer, e.g. hydroxyethyl methacrylate (HEMA), glycerol dimethacrylate (GDMA), etc. In the second type of RMGI system, the polymer is unmodified polycarboxylic acid. In this case, the liquid is formulated with a mixture of hydrophilic methacrylate monomers and water. Generally, the water content of these materials is lower and the monomer content higher than for the first type. As a result, the coefficient of thermal expansion of these glass ionomers is high. Free-radical initiators are added to trigger the curing of the methacrylate groups. Visible light initiators and/or self-cure redox initiators are employed to effect this curing and covalent cross-linking reaction.

Nature of the glass

The FAS glass of the RMGI systems is similar in composition to the glasses described for conventional glass ionomers, although some variations are made in order to match the refractive index of the glass with that of the matrix. It is also common to treat the surface of the glass with an organic modifier, such as a methacryloyl functional alkoxysilane, to allow better binding with the methacrylate matrix.

Two-paste versions

More recently, two-paste versions of the RMGI luting cements have become available to the clinician in convenient metered double-barreled dispenser

systems. This ensures accuracy of the ratio of the polyacid to the FAS glass and guards against the moisture sensitivity sometimes experienced by the powder of the earlier systems. In addition to the FAS glass, finely ground non-reactive radiopaque fillers, similar to those used in composites are incorporated to stabilize the aqueous paste containing the modified polycarboxylic acid. Proprietary redox initiators are added to trigger the polymerization of the methacrylate groups.

6.5.2 Mechanism of action

Setting reactions of resin-modified glass ionomers

Two distinct types of curing reactions take place in a true light-cured glass ionomer, the traditional acid–base glass-ionomer cure and the free-radical methacrylate polymerization (Mitra, 1994). In the laboratory, the former can be followed by infrared spectroscopy through the appearance of carboxylate ion peaks. The methacrylate reaction, being a chain polymerization, proceeds at a rate that is several orders of magnitude higher than the acid–base reaction. In practice, the extent to which each of these two reactions occur is very dependent on a particular system. If the system is low in water and high in the methacrylate components, the ionization of the polycarboxylic acid will be severely suppressed resulting in little acid–base reaction. In one system, the redox initiators are microencapsulated in inert components and mixed with the powder (Mitra and Mitra, 1991). When spatulated with the liquid, the initiators are triggered and free-radical polymerization of the methacrylate groups initiates. In some commercial RMGI luting cements an additional light-curing initiation is provided. However, light will polymerize only the cement exposed at the margins leading to a false sense of security since the bulk of the cement under the crown typically would take longer to undergo a clinical set.

Role of water and tartaric acid

As with conventional systems, water is an integral part of all true RMGIs, being essential for the acid–base glass-ionomer reaction to proceed to any appreciable extent and for the release of fluoride from the FAS glass by this mechanism. Tartaric acid may be optionally added to modulate the working time and acid–base glass-ionomer setting reaction.

6.5.3 Manipulation

RMGIs are easier to use than their conventional counterparts. The powder and liquid type are easier to mix since the surface energies of the treated

glass powder and the resin–polycarboxylic acid mix are more closely matched. The cement is considered properly mixed (usually within 30s) when it forms a string between the pad and the spatula about 25 mm long. Considerable variation occurs though between products from different manufacturers regarding the viscosity and consistency of the cement mix. A popular commercial RMGI cement has a mousse-like consistency which makes the placement of the material in the crown easier since the cement is readily scooped from the pad. Mixing of the two components is vastly improved in paste–paste systems, thus reducing operator variability and facilitating the attainment of optimal properties. Mixing time is shorter (usually 10–20s) than powder–liquid systems. The paste–paste RMGI cements are delivered through a convenient double-barreled dispenser called the ‘clicker’ (RelyX™ Luting Plus Cement, 3M ESPE) or the ‘paste-pack’ (Fuji™ CEM, GC Dental). It is important to remember that these are still water-based systems and the cap of the double-barreled dispenser should be securely replaced after each use to avoid loss of water and thickening of the pastes. Clean-up of the popular cements of this class is quite easy since excess cement can be removed when it is in a waxy stage. If a luting cement cures too rapidly and sets hard, the excess has to be removed with a sharper, more aggressive instrument. This may lead to chipping at the margin. This class of cement is neither as moisture-sensitive nor as prone to desiccation as the conventional glass-ionomer (Cho *et al.*, 1995).

6.5.4 Properties

As with conventional glass ionomers, the properties of RMGI luting cements are regulated under the ISO 9917-1:2003 standard for dental water-based cements and self-curing resin-modified cements.

Setting and working time

The working time is typically greater than 2.5 min from the start of mix at ambient temperature of 23 °C. Higher temperatures and vigorous spatulation shorten the working time while lower temperatures prolong it. Excess material can be removed when the cement reaches a waxy stage after placement in the mouth (2–3 min at 37 °C) using a suitable instrument. The restoration should be finished and the occlusion checked when the material has completely set (about 5 min from placement, depending on brand).

Solubility and erosion

RMGI luting cements have greatly improved resistance to dissolution when compared with zinc phosphate, polycarboxylate or conventional

glass-ionomer luting cements (Cho *et al.*, 1995; Donovan and Cho, 1999). The ISO 9917-1 erosion test for lactic acid shows the solubility to be virtually zero. This is one of the key advantages of this type of cement (Falsafi *et al.*, 2003a).

Fluoride release

Although differences exist between manufacturers' brands, in general, the fluoride release and rechargeability of RMGI luting cements was found to be similar to that of the conventional glass-ionomer cements (Ton *et al.*, 2006). The beneficial effect of fluoride from RMGIs has been shown *in vitro* (Nagamine *et al.*, 1997; Tantbirojn *et al.*, 1997) and *in vivo* (Donly *et al.*, 1999; McComb *et al.*, 2002; Haveman *et al.*, 2003). The dentinal caries inhibition of these materials due to sustained fluoride release was also reported to be similar to the conventional glass ionomers (Tantbirojn *et al.*, 2005).

Physical and mechanical properties

Both the early mechanical properties, as well as the 'matured' properties, of the RMGIs are much improved over the conventional glass-ionomer luting systems. The additional covalent cross-linking in the matrix due to the polymerization of the methacrylate groups contributes towards this effect. Thus, these materials are considerably less brittle and have significantly higher tensile strengths, flexural strengths and fracture toughness values than the corresponding conventional systems (Li *et al.*, 1995). The properties of one paste–paste system were found to be similar to those of the corresponding powder–liquid type (Falsafi *et al.*, 2003b). The modulus values are in general lower for the RMGIs (Smith, 1999) and fracture toughness is higher, contributing to the favorable clinical outcomes in high stress-bearing areas (Akira *et al.*, 2003). The combinations of these unique characteristics make the RMGIs particularly attractive when used as luting cements under crowns, since they can provide relief of stress created by masticatory forces. All the ultimate properties build up rapidly during the first 24 h and then increase slightly during the next 7 days. As with conventional systems, most resin-modified systems do not undergo significant decrease in mechanical properties over time due to fluoride release (Mitra and Kedrowski, 1994).

Adhesion

Several RMGI systems (e.g. RelyX™ Luting Cement and RelyX™ Luting Plus Cement, 3M ESPE) do not require any etching, priming or

conditioning of the tooth and thus can be considered as self-adhesive cements. Others, such as Advance™ (Caulk/Dentsply) and Fuji™ CEM or Fuji™ Plus (GC Dental), suggest the use of additional conditioning agents. Thus Fuji Plus Luting Cement is used with a 10:2 citric acid–ferric chloride etchant due to the more resinous characteristic of the cement (McComb and Nathanson, 1999). Clinical retention of crowns with the RMGI luting cements has also been found to be excellent in long-term clinical studies. The measured *in vitro* bond strengths of RMGIs are considerably higher than their conventional counterparts, although still not as high as resin adhesive–composite combinations. The failure is usually cohesive in the glass ionomer; hence, as with other glass-ionomer cements, the bond strength measurements are not true reflections of interfacial adhesion. The mechanism of adhesion is a combination of two factors:

- the modification of the dentinal smear layer and interpenetration of the dentinal tubules by the fluid cement followed by polymerization and entanglement with collagen fibers;
- ionic reaction of the polycarboxylate with the calcium ions of hydroxyapatite.

The first mechanism has been observed by confocal microscopy studies. The second reaction has been verified by Fourier-transformed infrared spectroscopic studies. The additional feature of increased stress relief afforded by these materials contributes to the long-term durability of the prosthesis. Numerous studies of superior *in vitro* performance, often similar to the high-strength resin cements, have been published (Thonemann *et al.*, 1995; Mitchell *et al.*, 2000; Cheylan *et al.*, 2002). A restoration adhesively cemented with an RMGI luting agent is more resistant to microleakage when compared with a non-adherent cement like zinc phosphate (Lindquist and Connolly 2001). The RMGIs appear to exhibit minimal microleakage similar to the performance of adhesive resin cements although the latter yield higher *in vitro* bond strength values (Thonemann *et al.*, 1995).

Post-operative sensitivity

Perhaps the most attractive reason why this class of cements was readily adopted in clinical practice is because the users of RMGI luting cements observed remarkably low post-operative sensitivity in their patients (Christensen, 1995; Hilton *et al.*, 2004). This is perhaps because these self-adhesive materials do not need the removal of the dentinal smear layer and are not as technique-sensitive as the conventional materials. The seal at the dentinal margin is very good; hence, hydrodynamic fluid flow or the ingress of bacteria do not appear to be a problem. Another factor that

may play a role (though a minor one) is that the RMGIs start out at a higher pH (lower acidity) and, hence, do not cause an adverse reaction on the pulp.

Film thickness and dimensional stability

Important differences exist between manufacturers' brands; hence, the user must select materials of this class with caution. Data on film thicknesses have shown good crown seating for RelyX™ Luting Cement (formerly Vitremer™ Luting, 3M ESPE) similar to Fuji™ I conventional glass ionomer (GC Dental) but a substantially higher thickness was noted for the hybrid cement Advance™ (Caulk/Dentsply) (Tan *et al.*, 1998). There has been concern about the volumetric expansion of RMGI luting cements although the actual amount of shrinkage and deleterious effect therefrom is very dependent on the brand. Because of the *in vitro* expansion observed, it has been suggested that this class of materials should not be used for luting all-ceramic crowns and posts (Miller, 1995). However, it is important to note that differences exist between different brands of materials categorized in this class. In a recent study involving In-Ceram™ and VitaDur™ Alpha (Vident, Brea, California), porcelain jacket all-ceramic crowns luted with several RMGI, conventional glass-ionomer and resin cements, only crowns cemented with Advance™ RMGI (Caulk/Dentsply) demonstrated fracture after two months (Leevailoj *et al.*, 1998). Similarly, Snyder *et al.* (2003) did not see any incidence of fracture of Procera copings cemented with Vitremer™ Luting Cement (now RelyX™ Luting Cement) or Fuji™ Plus RMGI cement. The reason for the differences between cements is to a great degree dependent on the toughness of the particular material in question. The cements that are more resilient have a better ability to dissipate stresses due to expansion (Li and White, 1999).

6.5.5 Clinical usage

RMGI luting cements are indicated for routine cementation of: PFM crowns and bridges to tooth structure, amalgam, composite or glass-ionomer core build-ups; metal inlays, onlays or crowns; prefabricated and cast posts. They are also indicated for cementation of copings made with all-alumina or all-zirconia cores and provide retention similar to adhesive luting cements (Palacios *et al.*, 2006). Retention of the all-ceramic crowns with RMGI cement was reported to be excellent and similar to that achieved with adhesive resin luting cements *in vitro* (Ernst *et al.*, 2005) and with zinc phosphate cements in a split-mouth randomized clinical trial (Jokstad, 2004).

6.6 Traditional resin luting cements

Resin-based luting cements have been available for some time. The early materials developed in the 1950s were primarily based on acrylic resin chemistry. More recently, however, resin cement development has been based on the adoption of the chemistry of resin composites and adhesives (Christensen, 1993).

6.6.1 Composition

The early acrylic cements consisted of a powder containing poly(methyl methacrylate) beads and inorganic fillers, and a liquid, which was primarily methyl methacrylate monomer. Setting occurred through the self-cure peroxide–amine-initiator system. Since the 1970s, resin cements have been formulated as two-paste systems and are based on dimethacrylate resin chemistry similar to that used in resin composites and adhesives. The two-paste systems are easy to mix and cure at ambient temperature. These cements rely on the acid-etching technique and dentine conditioning, similar to composite restorations, to achieve high bond strengths. Although the composition of the matrix of the two-paste systems varies from one commercial product to another, the resin is usually a mixture of dimethacrylate monomers, e.g. 2,2-bis[4(2-hydroxy-3-methacryloyloxypropyloxy)phenyl]propane, commonly referred to as bisGMA, triethylene glycol dimethacrylate (TEGMA), 4-methacryloxyethyl trimellitic anhydride (4-META), etc. The resin mixture is formulated into pastes by incorporating silane-treated inorganic fillers (60–70% by weight), similar to those used in composite restorative materials. Small quantities of fumed silica or high molecular weight oligomers or polymers may also be added to modify the rheological properties so as to provide the practitioners with optimum handling properties. Free-radical initiators are incorporated to effect the curing of the cements. The two-paste resin cements are often provided as dual-cure materials. One of the pastes contains a reducing amine and a photoinitiator system. The other paste contains a peroxide, usually benzoyl peroxide. In an interesting variation of the initiator system, the anaerobic cements begin polymerization only when the ambient oxygen supply is cut off after placement of the prosthetic device. This feature provides extended working and setting times and offers easy removal of excess materials. Examples of this type of cement are Panavia™ F2.0 and Panavia™ 21 (Kuraray Dental, 2007). Unlike the polycarboxylate cements and the conventional and resin-modified glass ionomers, these cements have no inherent adhesion to tooth structure. Hence it is essential that these cements be used with a dental adhesive or conditioning system in order to bond the prosthetic device to the tooth.

6.6.2 Setting reactions

The curing of the methacrylate groups in the dual-cured resin cements can occur when activated by visible light and/or through the free-radical redox polymerization initiated when the two pastes are mixed. This chemistry is similar to that of the peroxide–amine-initiated polymerization in self-cure composites.

6.6.3 Manipulation

Since the resin cements do not have inherent adhesion to dental tissue, the use of dental bonding agents is essential to obtain adequate bond strength of the cement to the tooth structure. In addition, the use of an etchant, e.g. 37% phosphoric acid gel, is recommended for several commercial products. As such, the use of these cements is somewhat technique-sensitive and multiple steps are required to achieve the desired results. As with composite bonding, moisture control is critical. The surface of the prosthetic device also has to be prepared by sand-blasting or chemical treatments, e.g. with a silane primer. Mixing of the two pastes of the cement systems is usually quite easy. Products that are dispensed through mechanical devices that ensure the delivery of equal amounts of the two pastes are subject to low variability. The newer cements have good rheological properties so that they are easy to place, do not slump and provide for easy clean-up after placement. Working time is 2–4 min while set time is 5–10 min. It is very important to clean up the cement within the window of time specified by the manufacturer, otherwise the cement sets very hard and the excess is extremely difficult to remove.

6.6.4 Properties

Setting properties

The working and setting times for resin luting cements are defined by specification ISO/DIN 4049:2000. According to this specification the working time is determined from the start of mix at room temperature and has a minimum value of 90 s. The set time defined by the ISO specification has a maximum value of 5 min. The actual clinical working time and set time are somewhat different however. For procedures that require the cement to self-cure it is advisable to clean up the margin 3–5 min after seating and then allow the cement to set undisturbed for 10 min from start of mix. For porcelain and pre-cured composite crowns, dual-cured cements are the preferred choice. In these cases, the margins should be light-cured for the length of time recommended by the manufacturer (usually 20–60 s).

Erosion

Not surprisingly, the resin cements are quite resistant to erosion in an acidic aqueous environment. The solubility in water is also very low (Table 6.3).

Adhesion and post-operative sensitivity

These cements require the use of resin bonding agents and acid-etching procedures. Laboratory measurement of bond strengths of various devices cemented with the resin luting cements to dentine yield the highest values among luting cements, typically in the 18–30 MPa range (Behr *et al.*, 2003). In practice, it is necessary to have adequate moisture control in order to achieve good adhesion clinically. Use of the acid-etching procedure, which removes the protective smear layer from the dentine, has been linked to a greater incidence of post-operative sensitivity experienced with resin luting cements (Donovan and Cho, 1999). The high incidence of post-operative sensitivity noted clinically with this class of cements was found to be eliminated when the teeth were lined with Vitrebond™ RMGI liner (Wat and Chang, 1995). The use of ceramic primers to treat the surface of machinable glass-ceramics and high-strength ceramics has been found to provide significantly improved bond strengths (Begazo *et al.*, 2004; Keiichi *et al.*, 2005).

Physical properties

The compositions of the resin cements are very similar to those of self-cured or dual-cured composites, therefore the physical properties are also equivalent to those of low-filled composites. In particular, the mechanical properties are significantly higher than any of the other classes of cements (Piwowarczyk and Lauer, 2003). This factor, coupled with the higher bond strengths, indicate this class of cements as the preferred materials for non-retentive preparation and for cementing non-metallic prosthetic devices.

Fluoride release

These cements possess no intrinsic fluoride release and, hence, have no anticariogenic benefit.

6.6.5 Clinical applications

The use of traditional resin luting cements requires several steps and adequate moisture control in order to obtain clinically successful results. These

cements are designed to be used with the corresponding resin bonding agents. When used in this manner high bond strengths are achieved. The combined systems are indicated for the cementation of esthetic indirect restorations including crowns, inlays and onlays composed of porcelain and all-ceramic or pre-cured composites. They are often regarded as being rather technique-sensitive because of their inherent polymerization shrinkage and sensitivity to moisture (Sorensen *et al.*, 1998). The need to use total-etch bonding systems often results in post-operative sensitivity. The use of many of the modern self-etch adhesive systems is contraindicated since their residual acidity inhibits the chemical curing reaction of the amine–peroxide redox initiator system of the cement. Light-curing of the cements is useful for bonding thin porcelain veneers where adequate penetration of light is not a problem. Since these cement systems have high bond strength, they are indicated for cementing indirect restorations composed of metal or PFM to preparations with minimal coronal tooth structure. Other limited applications of such cements include the cementation of endodontic posts, amalgam restorations and orthodontic devices, although in these cases specialized formulations are often made available.

6.7 Self-adhesive resin cements

The newest type of luting cement is the self-adhesive resin cement designed for adhesive luting of all-ceramic, metal or composite indirect restorations and posts including fiber posts. These greatly simplify the luting procedure needing only one application step (Duke, 2003; Radz, 2003). The first of this class of materials was introduced in 2002 as a powder–liquid material provided in unit-dose capsules that have to be triturated (RelyX™ Unicem, 3M ESPE, 2002). Since then other self-adhesive luting cements have been introduced in paste–paste dual-barrel delivery devices although a primer is needed for at least one material (Multilink™ cement system, Ivoclar-Vivadent, 2006).

6.7.1 Composition

The benefits of conventional and adhesive luting techniques have been combined in these materials by the incorporation of different components from many of the prior generations of materials classes. The first material of this class, RelyX™ Unicem (3M ESPE), contains a liquid consisting of phosphorylated dimethacrylate monomers similar to those used in self-etching bonding agents. The filler consists of a reactive FAS glass, similar to glass ionomers, and calcium hydroxide which can neutralize the acidic monomer during the setting process, to avoid hydrolysis, thus providing

long-term stability. The cement is dual-cured, i.e. it can be set by light initiation in addition to free-radical chemical curing. Proprietary redox polymerization initiators has been developed to provide curing of the methacrylate groups during the setting reaction. More recently, newer paste–paste versions have been commercialized. These are easier to use since they do not require trituration and are easier to mix. Several commercial systems where a static mixer is provided at the end of the syringe also provide additional convenience for the practitioner. Compositionally, the paste–paste versions additionally utilize inert silanized fillers on the acidic paste side while non-acidic methacrylate monomers are incorporated to formulate the second paste.

6.7.2 Mechanism of action

Important differences exist between different manufacturers' products in this category. For RelyXTM Unicem, the setting reaction predominantly involves radical polymerization which can be initiated by exposure to a dental curing light or through a redox-initiated self-cure mechanism and proceeds in the same way as setting reactions for dual-cured resin composite materials. Extensive cross-linking of the methacrylate monomers creates a dense hydrophobic network that is reinforced by silane-treated fillers resulting in a material that has high mechanical strength, minimal solubility and low water absorption. While still fluid the phosphate groups of the monomer dissolve the smear layer which allows penetration of the cement into the dentinal tubules, thus providing a good hybrid layer and strong adhesion. The use of basic fillers also ensures that the remaining acidic groups are neutralized, thus preventing the possibility of hydrolytic degradation of the set cement and ensuring long-term durability. The MultilinkTM system (Ivoclar-Vivadent, 2006) is self-cure only and requires the use of a primer system for adhesion.

6.7.3 Manipulation

The powder–liquid versions are supplied in capsules and are trituated in an amalgamator after activation, while the paste–paste versions can be hand-mixed after dispensing. Some manufacturers supply static-mixer tips through which the two pastes can be auto-mixed directly from the dual-barreled syringe into the crown preparation. Working time is about 2 min from the start of mix. For the dual-cured versions excess cement is conveniently removed after a brief light exposure of about 20s or during self-hardening after the gel phase is attained. Total set time after start of mix is about 5 min after start of mix.

6.7.4 Properties

Although this is the newest class of luting cements, these cements have been the subject of intense laboratory and clinical studies over the past few years since their inception. Most published studies are on Unicem™ cement, the first of this category. Understandably, the clinical history is short but the data so far are very favorable.

Physical and mechanical properties

The *in vitro* compressive strengths have been reported to be similar to traditional high-strength composite luting cements (Piwowarczyk *et al.*, 2002), while the stabilization of ceramic crowns against fracture was also found to be similar (Burke, 2003).

Adhesion

Numerous reports of the excellent adhesive qualities to both tooth structure and fixed prosthodontic materials have been published (Piwowarczyk *et al.*, 2004; Walter *et al.*, 2005; Escribano and de la Maccora, 2006). In one study, all-ceramic crowns were evaluated after bonding with Unicem and simulation of oral stress. Scanning electron microscopy showed amounts of perfect margin rating similar to traditional adhesively bonded luting cements (Behr *et al.*, 2004). In order to get optimum adhesion it is important to use the correct seating force on the crown with these cements to enable the cement to flow into the coronal dentinal structure after it is etched by the acidic phosphate monomer (Goracci *et al.*, 2006). The elimination of separate etching steps is a major advantage and is directly related to the remarkably low incidence of post-operative sensitivity and debonding (CRA Newsletter, 2003; Cobb *et al.*, 2004; Farah and Powers 2004). When bonding zirconia ceramics, pre-treatment of the prosthesis (such as sandblasting with alumina powder or tribomechanical coating with silica powder) has been reported to provide greater bond strength (Piwowarczyk *et al.*, 2005). Excellent success with adhesive bonding of this new class of luting cements to chair-side CAD/CAM inlays and onlays (Blatz *et al.*, 2006) has been reported.

Fluoride release

A few of these cements exhibit some fluoride release although the quantity of fluoride is quite low compared with conventional and resin-modified glass-ionomer cements.

6.7.5 Clinical usage

This class of materials are very versatile in their use and are indicated for final adhesive cementation of metal and PFM crowns, bridges, inlays and onlays, all-ceramic and composite prosthodontic devices, strengthened-core ceramic crowns and bridges, pre-fabricated and cast posts and pins as well as, more recently, a fiber-post system. The cementation of veneers is not indicated with some of these dual-cured systems. The simplification of clinical steps, extremely low incidence of post-operative sensitivity and early clinical success (Burke *et al.*, 2006) have quickly resulted in this class of cement gaining in popularity amongst clinicians.

6.8 Summary

The last two decades have seen several remarkable shifts in dental practice thanks to the rapid influx and assimilation of innovations in materials science and technology. As a result, contemporary dentists have many options available for consideration when choosing a luting cement. The choice of the cement, whether old or new, should depend on the particular clinical situation and specific criteria. While improved physical properties or *in vitro* adhesion strengths may be considered advantageous, they have not automatically resulted in improved clinical performance. Ease of manipulation and handling, cement clean-up and minimal technique sensitivity are important factors in ensuring clinical success. These factors – coupled with results of favorable long-term clinical studies including absence of post-operative sensitivity, long-term retention of the prosthodontic device and marginal integrity – should be the deciding factors that clinicians take into consideration while selecting the cement for a particular procedure.

6.9 References

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Mixed-methods approach to wear evaluation in posterior composite dental restorations

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7.1 Introduction

In vivo and *in vitro* wear evaluations of composites should be carried out in parallel in a single study, with a view to correlating the technical excellence of novel posterior composites and their clinical wear behaviour. Intra-oral wear tribology of dental composites is a cumulative effect of abrasion, erosion and bio-tribocorrosion where the effects of patient factors on the material wear are critical (Lambrechts *et al.*, 2006). Clinical tools in qualitative *in vivo* wear studies do not quantify wear (Taylor *et al.*, 1989) but rather try to identify contributory patient factors (Vrijhoef *et al.*, 1986; Söderholm *et al.*, 1998). A more sophisticated approach is the application of quantitative *in vivo* wear studies to report the link between the material properties (Söderholm *et al.*, 2001) and wear magnitude.

Unfortunately, qualitative and quantitative approaches are seldom combined and their respective strengths are ignored across traditional methodological boundaries. This trend is probably because researchers are often taught to master only one type of method and, so, become comfortable with their expertise in handling either qualitative or quantitative analysis, but not both. The inherent danger in this strict separation of research perspectives will be the likely failure to validate the technical excellence of novel composites in general practice settings.

In an attempt to encourage researchers to conduct combined-method investigations in wear research, this chapter will:

- discuss the methodological basis of qualitative and quantitative approaches to wear research in posterior composite restorations;
- assess and address specific points of critique of both approaches and argue the case for combining both to maximise analytical leverage.
- present a case study to describe how both approaches can complement rather than compete with each other.

7.2 Qualitative methods of wear evaluation

Qualitative research methods, in general, are most often associated with inductive approaches. Inductive research begins by making observations, usually in order to develop a new hypothesis or contribute to new theory, or to look for patterns and processes that answer ‘how and why’ questions. Qualitative research in wear is perceived as a method for using narrative description in the form of observations and constant comparison, so seeking a better understanding of the complex phenomenon of wear. Clinical trials appraise the wear of materials in clinical service by observing their degrees of deviation from the ideal aesthetic and functional properties of enamel, which is the replaced or restored tooth tissue (Lambrechts *et al.*, 1989). Such qualitative clinical research studies on the wear of posterior composite restorations have used inductive approaches in both retrospective and prospective evaluation.

In the past, very few observational clinical trials that have considered resin composite restorations (Crabb, 1981; Elderton, 1983; Paterson, 1984) have used patient records of dental treatment in the retrospective evaluation of wear. However, this type of evaluation has been criticised because the studies do not take into consideration the many variables such as quality of the restoration, patient oral hygiene and dietary habits, materials used and placement conditions (Marynuik, 1984). Retrospective cross-sectional studies differ from controlled longitudinal investigations, in which selected clinicians treat selected patients under almost ideal conditions for the materials investigated (Hickel and Manhart, 2001).

Recent clinical trials on prospective evaluation of wear of posterior composite restorations have adopted rating scales both *in vivo* and *in vitro*. Rating scales offer the possibility of producing meaningful clinical information, rapidly and inexpensively, reflecting the aesthetic and functional performance of restorations fabricated from a variety of dental restorative materials. The use of clinical rating scales (*in vivo*) for evaluating wear of posterior composite restorations in a standardised way dates back to the early 1970s, following the publication of the Ryge, or United States Public Health Service (USPHS) system criteria (Cvar and Ryge, 1971; Ryge and Snyder, 1972). The scanning electron microscopy (SEM)-supported micro-morphologic replica technique was introduced for the evaluation of posterior composite restorations, two decades ago. With the advent of this technique, material loss is coded (*in vitro*) with great sensitivity on the occlusal surfaces and the tooth–restoration interface to parallel the clinical coding, in order to assess qualitatively the longitudinal wear behaviour of restorations.

7.2.1 United States Public Health Service system

Ryge and Snyder (1972) provided a clinically meaningful approach for evaluating the clinical performance of restorative materials three decades ago. Since then, most of the existing information on composite restoration wear from prospective studies has been based on this universally accepted systematic approach.

Rationale for using the United States Public Health Service system in wear evaluation

The system uses a grading concept based on subjective observations of such parameters as colour-matching ability, marginal adaptation, recurrent caries, loss of anatomical form, post-operative sensitivity and retention rate. The restorations are graded for these parameters in order to assess the outcome of material wear in aesthetic (colour-matching ability, loss of anatomical form, roughness), functional (retention, marginal adaptation) and biological properties of the material (recurrent caries, post-operative sensitivity). Surface roughness induces surface staining, further influencing the colour match and translucency of the composite restorations compared with the neighbouring enamel surface. Wear alters the occlusal anatomy initially and in long-term clinical service by fatigue, eventually degrading the functional properties of the material through marginal and catastrophic bulk fractures. Recording the pulpal response to restoratives is important for failure analysis of restorations in clinical wear studies.

Method of data collection

For each USPHS parameter, there are a range of scores (rating scales) from Alpha (perfect) to Delta (failure), with clear descriptions of what clinical factors are included for each score. Restorations should be replaced with a grade of 'Charlie', i.e. the restoration has failed. The rating scales were specifically designed for comparing two different dental materials or two different dental procedures involving the same patient. The patient thus serves as his or her own control. Training and testing of examiners for an acceptable performance of 85% intra- and inter-examiner variability is mandated. Two trained examiners and one recorder are required to perform this procedure. When the first examiner has evaluated both members of the pair, the second examiner takes his turn. If both examiners agree, the rating becomes final; if they do not agree, the recorder requests that a joint examination be conducted, and that the examiners agree on a final rating. While the USPHS methodology has served us well, a few issues remain unsolved.

Limitations

- Current restorative materials have vastly improved clinical performance and any changes over time are not easily detected by the limited sensitivity of the Ryge criteria in short-term clinical investigations (Taylor *et al.*, 1989).
- Many researchers have modified the criteria for their own study needs (Allander *et al.*, 1989). Consequently, insensitivity, combined with the continually evolving and non-standard investigator modifications of the categories and scales of original Ryge methods, might well lead to the misinterpretation of many judgements as good clinical performance.
- As this method requires an accurate calibration of the examiners (Ryge *et al.*, 1981), several researchers (Hickel and Manhart, 2001; Burke *et al.*, 2002; Mjör and Gordan, 2002; Manhart *et al.*, 2004) pointed out the difficulties of applying the method in daily practice, where clinicians are not calibrated.
- The inconsistent application and intentional variations incorporated in the grading procedure may seriously weaken the study and are likely to introduce bias, e.g. the use of the criteria by one examiner-operator as opposed to the two independent non-operators that are recommended. However, these assumptions have not been validated.
- The criteria for failure are not specific, due to both ‘Charlie’ and ‘Delta’ relating to an unacceptable restoration. Since the reasons for the clinical choice of repairing or replacing a restoration are often not validated, it is common for different practitioners to exercise their judgement in line with certain written criteria without any efforts to check on inter-observer (or even intra-observer) variation.

7.2.2 Micro-morphological feature analysis

In recent years, the application of SEM for characterisation of the micro-structure of posterior composites *in vivo* and *in vitro* has increased. In general, morphological information, such as filler morphology and filler content, as well as surface information such as texture and roughness parameters of restoration surfaces, can be obtained with SEM. Specifically:

- SEM complemented with high-magnification optical microscopy can assess the composite-specific micro-morphologic *in vivo* behaviour of the restoration material by characterising excess of material after application, occlusal contact area wear (OCA wear), contact-free occlusal area wear (CFOA wear), micro-gap formation and fatigue cracks;

- a qualitative SEM fracture analysis in dynamic *in vitro* studies, aids confirmation of continued degradation at the filler–resin interface of resin composites (Lin *et al.*, 2000);
- the SEM digital imaging technique enables the *in vitro* development of profile maps for resin-based composites to make valid correlations between the filler particles within a composite and wear, since the size and characterization of filler particles have also been considered to be significant factors in the rate of wear of composites (Jaarda *et al.*, 1993).

Rationale for analysing the micro-morphology of composites in wear evaluation

While loss of material in restoration margins is an important entity for *in vivo* evaluation of the wear behaviour of composites, it should be evaluated separately and differentiated from occlusal wear. Such differentiation is difficult in clinical evaluation due to the presence of overhangs along the margins and can be better detected on replicas by means of SEM. *In vitro* SEM characterisation of the resin matrix microstructure and filler particle distribution of composites enables the correlation of micro-morphology with wear resistance.

Method of data collection

Selection of samples depends on the objective of the study and proper sample preparation is the key to measuring high-quality data with SEM, as with any other electron microscopic technique. Previous studies have demonstrated the use of epoxy dies obtained with indirect replication techniques (Ekfeldt *et al.*, 1995) in SEM examination, for the *in vivo* assessment of composite material loss at occlusal surfaces and margins (Roulet *et al.*, 1991), and the use of a suspension of filler particles in an *in vitro* study of composite resin micro-morphology (Jaarda *et al.*, 1993). The art of sample preparation for *in vivo* and *in vitro* studies is in fact a simple procedure of critical steps, where each step is indispensable for precise morphological determination and unambiguous particle characterisation.

A common preparation technique for *in vivo* studies is to first mount clean, completely dried epoxy replicas on sample holders or stubs and subsequently coat the samples with a nanometre layer of conductive material, such as gold, from a sputtering machine in a vacuum chamber. Although impressions are cast in fine stone in clinical use, stone is inappropriate for use with SEM as it lacks details and cannot withstand the procedures necessary for specimen production. This problem may be overcome by casting using a low-viscosity, cold-cure acrylic resin

(Araldite-D, Ciba Geigy, Belgium), which is capable of withstanding the desiccation and vacuum necessary for SEM viewing. Gold or carbon coating renders the surface conductive for viewing in the scanning electron microscope. Evaluation of prepared, coated replicas obtained at baseline and recalls thereafter are viewed under high-magnification optical microscopy (OPMI PRO ergo, Carl Zeiss Surgical GmbH, Germany), after subdividing the occlusal surface of each tooth into four quadrants. SEM views of each quadrant of the acrylic casts can then be obtained as photomicrographs for further qualitative interpretations such as longitudinal micro-morphologic wear (Gaengler *et al.*, 2001) and marginal behaviour (Gaengler *et al.*, 2004).

In vitro wear studies to relate the filler composition and resin morphology to wear rate use a wash–centrifuge–dehydrate–mount–coat protocol. Subsequent to the elimination of unpolymerised monomers by a washing technique (Lang *et al.*, 1992), the composite material is dissolved in acetone and centrifuged. The remaining filler particles including the pre-polymerised fillers are then placed in absolute ethanol and the suspension of filler particles is smeared on a glass slide, dried and gold-sputtered in vacuum, to perform morphological examination using SEM.

Limitations

- Barnes (1978, 1979) and Ekfeldt *et al.* (1985) have presented reviews of replication techniques and SEM. Artefacts are frequently seen when replicas are studied using SEM and, unless recognised, may lead to misinterpretation and render the eventual SEM photograph useless as a research tool.
- Loss of surface detail may be due to faulty impression techniques, inadequate mixing, or removal of the impression before setting is complete. The use of a standardised technique to obtain the impressions and the use of a skilled operator for SEM specimen preparation and viewing can possibly limit these problems.
- Surface detail may also be lost in casting due to use of material beyond its shelf-life or incorrect handling and manipulation of material containing air bubbles. This can be controlled as far as possible by the SEM technician.
- The samples to be evaluated by SEM are subjected to adverse conditions inside the equipment, such as high vacuum and high temperature. This may influence the evaluation of the sample, making small defects on the surface of the specimen more pronounced.

When the question of qualitative assessment of restorations is of concern, the patient's opinion of a restoration – which includes satisfaction with

aesthetics, tooth sensitivity, surface texture and contour – should be of primary interest. Comprehension of the tribological basis of the wear observed, the clinical rating in patients and the micro-morphology of composites can be aided by the following:

- dental history to explore the patient's satisfaction with their restoration(s) over time;
- medical history (e.g. general illnesses, long-term medication, injuries, traumata, evaluation of the patient's general condition);
- behavioural history (e.g. dietary and oral hygiene habits, smoking, inability or unwillingness to cooperate).

7.3 Quantitative methods of wear evaluation

Quantitative research methodology is based on deductive approaches. Deductive research begins with pre-specified hypotheses focused on testing preconceived or known theories. Quantitative methods to evaluate wear are predominantly indirect methods using impressions and casts to measure the vertical loss of height and volume loss of resin composite restorations. They are based either on visual evaluations made by the dentist or on physical measurements made by machines. Irrespective of the methodology, a restoration's wear resistance should be quantified in relation to that of enamel (Lambrechts *et al.*, 1989). Different quantitative techniques have been used in dentistry to quantify the wear of resin-based composites such as: volumetric techniques, grading systems and mechanical – leading to – digitised scanning procedures.

7.3.1 Volumetric procedure

The University of Minnesota (or UMN) technique is a surface evaluation technique for quantitative measurement of wear to determine the volumetric loss of material (Peters *et al.*, 1999).

7.3.2 Grading system methods

Leinfelder developed a semi-quantitative or discrete, qualitative method (Eick, 1985) describing a generalised system that takes into account the entire periphery of the restoration. This method (Leinfelder *et al.*, 1986) estimates progressive wear in replicas compared with a series of calibrated standard casts that demonstrate an increasing severity of wear at approximately 100 µm.

The method developed by Moffa–Lugassy (Lugassy and Moffa, 1985) consists of an M–L scale using 18 calibrated standard casts to estimate the

early stages of wear in replicas at 25 µm increments. The Vivadent or the Rheinberger scale (Bryant, 1990) is a combination of the Leinfelder and M-L scales. It consists of a series of ivory tooth-sized replicas to estimate incremental wear ranging from 25 to 1000 µm.

7.3.3 Mechanical procedures

Some metric devices measuring the heights of the exposed cavity wall (Kreulen and Amerongen, 1991) provide an objective quantification of wear. Examples of mechanical procedures using metric devices include the following: stereomicroscopy (Jørgensen and Asmussen, 1978); laser interferometry (Atkinson *et al.*, 1982); three-dimensional (3D) microscopy (Lambrechts *et al.*, 1984; Adams and Wilding, 1988); 3D optical scanners (Mehl *et al.*, 1997); Moiré contouring (Mayhall and Kageyama, 1997); contacting laser profilometry (Bartlett *et al.*, 1997); or the use of mechanical sensors such as LVDT (McDowell *et al.*, 1988) or extensometers (Lutz *et al.*, 1979; DeLong *et al.*, 1985). A radioisotope technique has also been described (Glentworth *et al.*, 1984).

7.3.4 Digitised scanning procedures

Digital mapping methods

Digital mapping of tooth surfaces seems to be the most precise method of scanning, with better accuracy for indirect wear measurements. According to Perry *et al.* (2000), three techniques appear to achieve a high level of accuracy. These digital mapping methods include the system developed by Clinical Research Associates (CRA) (Bangerter *et al.*, 1987), the Minnesota system (Roulet, 1987) and the 3D laser digitizing method or 3D laser scanning (Roulet *et al.*, 1983). The high level of accuracy in 3D data acquisition rendered by the high-precision laser, the simplicity of the method and the short measuring time justifies the preferred use of 3D laser digitizing methods in larger clinical studies.

Scanning electron microscopy quantification procedures

Clinical studies have proven the use of SEM in ‘quantifying’ the material loss at composite restoration margins (Roulet *et al.*, 1989; Heintze *et al.*, 2000; Gaengler *et al.*, 2001). SEM has also proven useful to demonstrate ‘quantitatively’ the filler particle content in terms of number, sizes and area occupied by filler particles in correlating the filler content to the wear behaviour of resin-based composites (Jaarda *et al.*, 1993).

Limitations of visual and mechanical techniques

The grading system using visualisation techniques involves the categorisation of replica models by comparison with a set of standard casts. The method, being simple and precise, makes the evaluation of models simpler and more precise than a clinical evaluation (Kreulen and Amerongen, 1991). Despite its simplicity, the grading system has the disadvantages that only discrete steps in wear can be evaluated (Mehl *et al.*, 1997) and it requires good calibration. In addition, regardless of the type of the mechanical device used, all seem to present measuring-device restrictions (Lambrechts *et al.*, 1984) and can achieve high accuracy or ease of use but never both requirements at the same time (Hewlett *et al.*, 1992).

In the light of the limitations of visual and mechanical methods, without doubt the best method for quantifying wear is 3D laser scanning technology with SEM as an adjunct. In addition, sophisticated 3D scanning with an accurate, precise and reproducible measurement technique is recommended for the scientific quantification of wear in contemporary restoratives (Hickel *et al.*, 2007).

Three-dimensional laser scanning: rationale

Three-dimensional scanning of the entire occlusal surface of the restoration is a measurement technique with high reproducibility in the micrometre range for measuring both clinically relevant parameters for wear quantification, i.e. vertical loss at OCAs and volume loss along the entire occlusal surface. Evaluation of the wear resistance of restorative materials in clinical service requires that quantification of both parameters is essential, since the vertical loss is a measure of OCA wear and the volume loss is a measure of bio-tribocorrosion. Since enamel-like wear resistance is one of the major requirements for posterior resin composites, the technique enables the comparison of OCA composite wear with enamel facet wear and can be used to record the differential wear (OCA composite wear minus enamel wear) at the same facet.

Method of data collection for digitised scanning procedures

Three-dimensional images are made by scanning a laser beam, under computer control, over the replicas, with multiple reflected surface points optically detected and recorded using a charge-coupled-device (CCD) chip, which is integrated with the host computer. The captured surface topography of the follow-up images is superimposed over baseline images and the aligned surfaces are subtracted with image analysis software to reveal changes over time. Using digital subtraction, the total substance loss is determined for the entire restoration surfaces as average loss

(mean), as well as along the margins on dentine and enamel as maximum depth of the area (0.5% quantile) at an accuracy of 10µm (Mehl *et al.*, 1997). The total substance loss reported as the total volume in cubic millimetres is recorded as the total occlusal surface loss of the replica, in addition to the measured vertical loss at OCA enamel, OCA composite and CFOA in micrometres. The average wear rate is calculated for the composite and referenced enamel at the OCA with subsequent differential wear calculations (compared with enamel). The results can be statistically analysed by considering each subject with restorations as a statistical unit and the multiple restorations placed in one subject should be regarded as dependent upon one another as the influence of the individual subject may play a crucial role. The null hypothesis that there is no statistically significant difference between the materials can then be accepted or rejected with the sign test at a confidence level of 95% ($P = 0.05$).

Quantitative scanning electron microscopy: rationale

Material loss at margins should be assessed quantitatively as a proportion (e.g. 25%) of the total length of the margin and should be differentiated as being located on the occlusal or proximal part of the restoration. A satisfactory correlation between the clinical criterion defining marginal discoloration and the SEM quantification has to be established.

Method of data collection for quantitative scanning electron microscopy

In this technique, a semi-quantitative clinical evaluation (SQUACE) to quantify marginal deterioration (Heintze *et al.*, 2000) is combined with SEM quantification of the proportion of degrading margins to differentiate materials loss at margins and cavo-marginal discoloration. The restorations are evaluated with the SQUACE method by making sketches of restorations on an evaluation sheet and using different coloured pens to trace the outline and mark the quality of the margin according to defined criteria. Subsequently, epoxy replicas from the impressions are prepared for SEM viewing as described previously. Using a comparative light microscope, the replicas are aligned and mounted identically in the scanning electron microscope for longitudinal studies. The length of the restoration margin is measured by tracing the margins on the scanning electron microscope screen with a digitiser and an interface. The traced length is simultaneously assessed for margin quality and assigned with corresponding criteria. The tracing and assessment is carried out for every sample and the percentage distribution of the quality criteria for each restoration is then calculated. The percentage distributions of both methods are

correlated and statistical tests are subsequently performed to accept or reject the null hypothesis.

7.4 Integrating diverse methods

Qualitative methods generally assess the clinical performance of materials and quantitative methods can only provide evidence of technical excellence for wear resistance of materials. It follows that there are fundamental differences between quantitative and qualitative wear research outcomes regarding the assessment of materials for wear resistance. Unless these two research paradigms are combined or mixed in a single study, the operational consequences of the presence or lack of technical excellence of materials cannot be assessed in the context of the oral environment.

Collaborating across traditional boundaries

In order to mix or combine research strategies in an effective manner, researchers first need to gain an understanding of the strengths and weaknesses of quantitative and qualitative research and to use what Johnson and Turner (2003) call the ‘fundamental principle of mixed research’. According to this principle, researchers should collect multiple data using different strategies, approaches and methods in such a way that the resulting mixture or combination is likely to result in complementary strengths and non-overlapping weaknesses. The effective use of this principle is a major source of justification for a mixed-methods approach in wear research, because the product will be superior to single-method studies. Tables 7.1 and 7.2 are specifically designed to aid in the construction of a combined qualitative and quantitative research strategy. After determining one’s research question(s), one can decide whether mixed research offers the best potential for an answer; if this is the case, then one can use the tables as an aid to help in deciding on the combination of complementary strengths and non-overlapping weaknesses that is appropriate for a particular study. Table 7.3 shows some of the strengths and weaknesses of mixed-methods research, which should aid in the decision to use or not use a mixed-methods research approach for a given research study.

Clarifying differences and acknowledging similarities

Although there are many important paradigmatic differences between qualitative and quantitative research, some similarities between the various approaches are sometimes overlooked. For example, both quantitative and qualitative researchers use empirical observations with statistical power

Table 7.1 Strengths and weaknesses of qualitative research methods**Strengths**

- Qualitative methods focus on assessing specific features of restoration wear (e.g. anatomic form, marginal degradation) rather than general state of the restoration.
- The results provide evidence for wear hypotheses (e.g. relation between wear resistance and micro-morphology).
- Conducting research in a controlled environment enables the researcher to reduce confounding variables (patient and operator factors) allowing one to assess more credibly material-and-wear relationships.
- The methods (grading systems) attempt to score the performance of materials as acceptable or unacceptable, addressing 'safety' and 'efficacy', rather than ranking.
- Results can describe the wear phenomenon of materials in the context of the oral environment.
- The researcher (in clinical wear studies) identifies the patient's opinion of a restoration including satisfaction with aesthetics, tooth sensitivity, surface texture and contour, which are related to the phenomenon of wear.
- The researcher (in SEM studies) can study the dynamic processes of wear (i.e. observing fatigue crack growth and propagation).
- Qualitative approaches generate an explanatory theory about the wear phenomenon (e.g. relating CFOA wear to the nature of the resin matrix).

Weaknesses

- Data collection is time consuming when compared with quantitative research.
- The results are more easily influenced by the researcher's personal biases, patient factors and idiosyncrasies.

Table 7.2 Strengths and weaknesses of quantitative research methods**Strengths**

- Testing and validating already constructed theories (e.g. wear and fatigue theory, protection theory) of how (and to a lesser extent why) wear phenomena occur.
- Testing wear hypotheses (Is new material as wear resistant as enamel?) that are constructed before the data on material wear are collected.
- Conducting research in a controlled environment enables the researcher to reduce confounding variables (patient and operator factors) allowing one to assess more credibly material-and-wear relationships.
- It provides quantitative, precise, numerical data on wear, enabling ranking of the *in vivo* performance of materials.
- Data collection using quantitative methods is relatively quick (e.g. automated mechanical devices with computer software).
- The research results are relatively independent of operator-induced bias (perceptual and judgement variations).
- It is useful in rapid and credible assessment of wear behaviour of materials in larger clinical trials.

Weaknesses

- Quantitatively evaluates wear assessment parameters for technical excellence, without appraising the clinical performance in general practice.
- Results of quantitative wear research are less likely to be used by general dental practitioners, since these require knowledge of statistics and research methodology.
- Research methods are less than ideal for general dental practice-based research due to lack of access to expensive mechanical devices and training in methodology.
- Inherent errors such as mechanical device restrictions, errors induced during sample preparation techniques, difference in standardisation and calibration of procedures.

Table 7.3 Strengths and weaknesses of mixed-method research

Strengths

- The clinical observational (qualitative) studies can be used to generate hypotheses of wear behaviour of materials and the quantitative studies can be used to test and validate the generated hypotheses.
- The validity of results can be strengthened by using more than one method to study the same phenomenon. This approach – called triangulation – is most often mentioned as the main advantage of the mixed-method approach.
- Results of qualitative wear research can help explain the quantitative material loss.
- It can provide qualitative and quantitative research strengths.
- The researcher can answer a broad and more complete range of research questions on wear, because the research is not confined to a single method or approach.
- The methods (grading systems) attempt to score the performance of materials as acceptable or unacceptable, addressing ‘safety’ and ‘efficacy’, rather than ranking.
- The researcher can use the strengths of an additional method to overcome the weaknesses in another method by using both in a research study.
- Can add insights and understanding that might be missed when only a singular method is used.

Weaknesses

- Can be difficult for a single researcher to carry out both qualitative and quantitative research, especially if two or more approaches are expected to be used concurrently; it may require a research team.
- Researcher has to learn about multiple methods and approaches and understand how to mix them appropriately.
- More expensive.
- More time consuming.

to address research questions. Both methodologies describe the wear phenomenon, construct explanatory arguments from their clinical (subjective) and laboratory (objective) data, and speculate about why the materials differ in their wear resistance. Additionally, both sets of researchers incorporate safeguards into their inquiries in order to minimise confirmation bias and other sources of invalidity that have the potential to exist in every research study. When the objectives, scope and nature of inquiry are consistent across methods and across paradigms, researchers and research methodologists need to be questioning when each research approach is most helpful; also, when and how they should be mixed or combined in their research studies. Greene *et al.* (1989; cited by Creswell, 1994) advanced five reasons why a researcher should mix methods and/or integrate methodologies: one of them being triangulation. This involves reviewing and analysing evidence from multiple sources such that a study’s findings are based on the convergence of that information (Erlandson *et al.*, 1993; Yin,

1994). The strength of the triangulation process lies in its capacity to neutralise any bias inherent in a particular data source, investigator or method when used in conjunction with other data sources, investigators and methods.

7.4.1 Data triangulation study design for mixed-methods wear research

The triangulation design model of mixed methods in wear research can be seen as a third research paradigm that is needed to reconcile and bring together the qualitative (USPHS, SEM, clinical photos) and quantitative (vertical and volume loss assessed by digitised scanning) data. The intent of this model is ‘data triangulation’ – to triangulate or gather both quantitative and qualitative data at the same time, and to integrate the two forms of data to best comprehend the phenomenon of wear. The insight and information gained in this manner can then be applied to materials evaluation and application. This model typically gives equal priority to quantitative and qualitative data and analysis (often found in separate sections of the report), involves concurrent or simultaneous collection of data and integrates both quantitative and qualitative data in the results, interpretation or conclusion phase.

A typical structure for a triangulation study is to have separate sections on quantitative data collection and qualitative data collection, as well as separate sections on quantitative data analysis and qualitative data analysis. The investigators then provide a results, discussion or conclusion section in which they discuss the results of both analyses. Typically, investigators present the two forms of results as supporting or conflicting evidence for results, or they might transform one type of data into another form (e.g. quantify the percentage of Alpha scores of the USPHS system) to converge results.

An example of how a triangulation model of mixed-method approach can help researchers to evaluate better the clinical wear performance of materials is outlined in the following case study. This is an attempt to promote the use of such an approach within the context of wear research.

7.5 A case study – spanning paradigms and combining methods

The case study involves a mixed-methods approach for wear assessment of novel posterior resin composites in a three-year prospective randomised controlled clinical trial. Table 7.4 provides an overview of the case study.

Table 7.4 Overview of the case study

Null hypothesis	Evaluated parameters	Rationale	Methods used
Quantitative: new material is as wear resistant as enamel	Vertical loss at OCA, volume loss at OCA and CFOA, marginal degradation	1 Vertical loss is a measure of contact wear and volume loss is a measure of contact-free wear. 2 Enamel-like wear resistance is required for restorative materials.	3D laser scan
Qualitative: new material shows an acceptable clinical performance, similar to that of traditional material	USPHS criteria, pitting and plucking, cracks	To test the 'safety' and 'efficacy' of materials by scoring their clinical performance as passing or failing to meet the international acceptance programme guidelines.	USPHS system, clinical picture documentation, optical microscopy, SEM

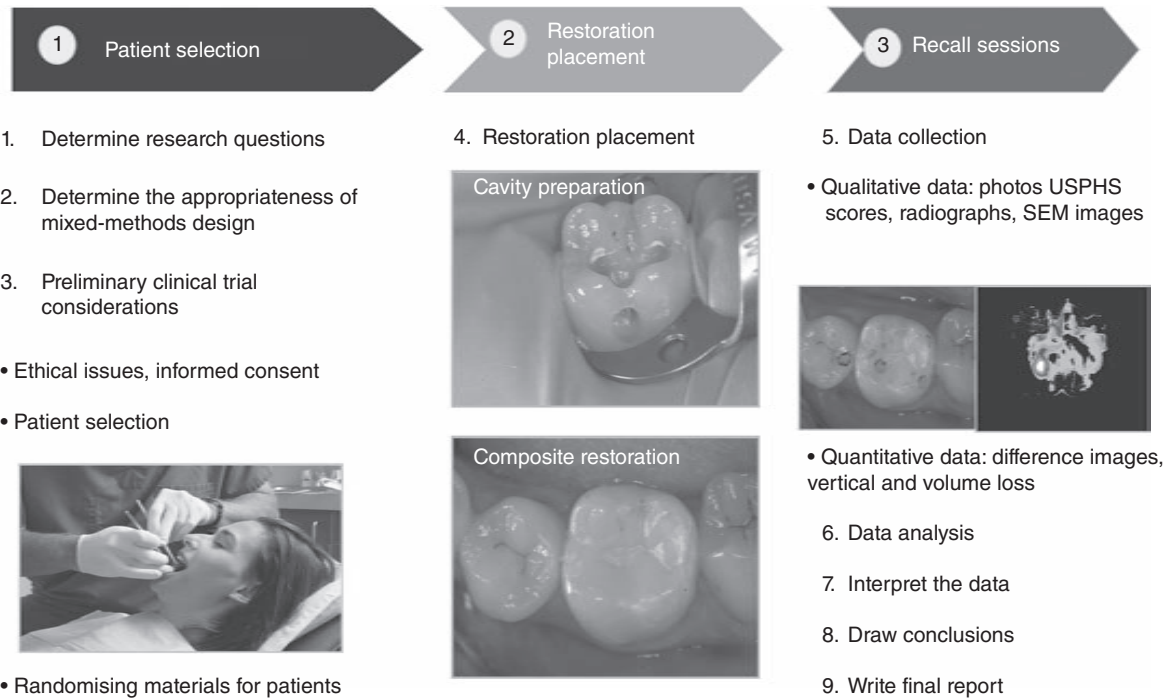
The proposed mixed-methods approach comprises nine distinct steps carried out in three major phases that are outlined in Fig. 7.1. The preparatory phase has its own set of procedures that should be followed in order to ensure an efficient course and conclusion to the trial. This is the planning phase including: defining the rationale, design and methodology of the study, patient screening, randomisation and preparation of the Clinical Trials Agreement, Patients' Informed Consent and Case Report Forms. The restorative phase is the phase of trial execution. During this phase, cavities are prepared according to a standard protocol and restoration of cavities takes place adhering to strict, manufacturer-directed protocols. The recall phases are important study visits, when each restoration is evaluated with USPHS criteria for signs and symptoms of wear and fatigue, complemented with bitewing x-rays, followed by registration of impressions and clinical picture documentation. The sequential procedures of the restorative and recall phases of this case study are represented in Fig. 7.2.

7.5.1 Preparatory phase

The design and writing of the clinical trial protocol, is followed by approval by the local ethics committee. Subsequently, the patients are screened after informed consent has been given and complete information provided on the study set-up and study goals. At the initial examination, a comprehensive dental, medical and behavioural history is recorded in association with clinical examination for dental caries and soft tissue examination for pathology. The inclusion of dental, medical and behavioural histories in the preparatory phase provides additional focus on the patient-related factors rather than exclusively investigating the material performance. Subjects are also evaluated for pre-operative sensitivity of the teeth to be treated. Dental bitewing radiographs of each tooth selected for the study are taken at the initial appointment to evaluate the extent of potential proximal caries. Following the screening, the study population is selected based on a set of inclusion and exclusion criteria. Such pre-defined criteria coupled with randomisation of subjects and establishing different operators and evaluators can effectively control the confounding variables avoiding bias and standardising the study design. Table 7.5 shows a sample set of inclusion and exclusion criteria for selecting the study population in a clinical trial on posterior composite restorations. The sample size of the study population should conform to American Dental Association acceptance guidelines (American Dental Association, 2001). According to these guidelines, a sample size greater than 20 will be required to demonstrate a statistical power, subjects of the study population can have not more than three restorations of a given type per subject and a minimum of 40 restorations in 20 patients must be evaluated after three years for each trial.

7.5.2 Restorative phase

The use of a paired ('split-mouth') design is encouraged in clinical trials, where each subject receives the so-called 'experimental restoration' as well as a 'control' restoration. A standard cavity preparation protocol with a strict placement technique according to the manufacturer's instructions is followed by adequate finishing and polishing procedures. Intraoral colour images of the selected teeth are taken before cavity preparation, after cavity (and where needed bevel) preparation, and after final finishing of the restoration (with and without occlusal foil). This will allow better determination of the restored tooth portion versus the unaltered peripheral enamel surface for further mapping and image analysis.



7.5.3 Recall phase

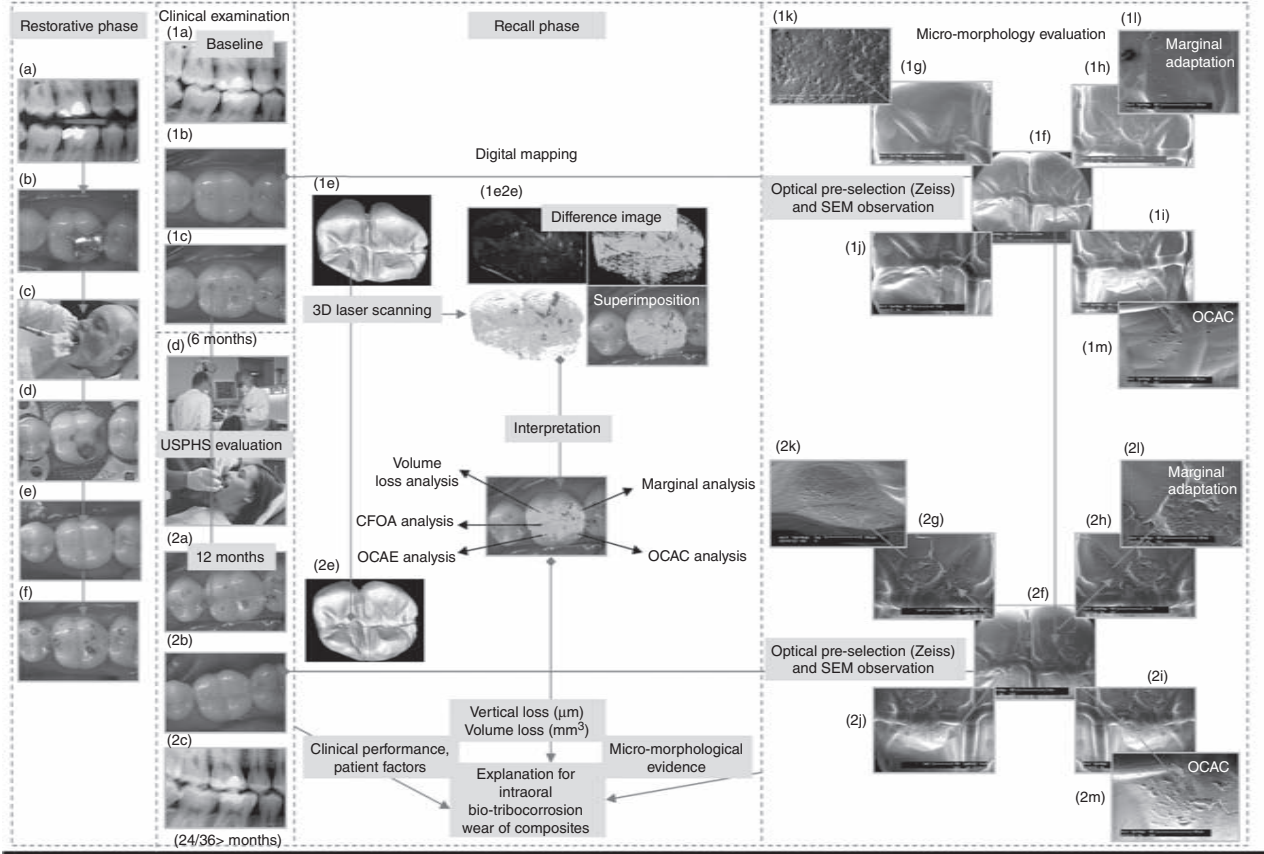
The recall period of three years is split into baseline – this means after 1 month of clinical service (in order to allow running-in wear for occlusal adaptation) – and 6, 12, 24 and 36 month recalls. During each recall, qualitative and quantitative wear data are collected and subsequently analysed, interpreted and eventually triangulated to evaluate the wear performance of materials in the study as acceptable or unacceptable (or to accept or reject the null hypothesis). A series of steps, as evident in Fig. 7.1 needs to be carried out at every recall phase.

Data collection

The ‘data triangulation’ concept of the mixed-methods approach is introduced at this step. A researcher might use ‘within-method triangulation’ (mixing methods within the same research paradigm) or ‘between-method triangulation’ (mixing methods across different research paradigms). The



7.1 Illustration of the nine steps carried out at three major phases of the case study. The study begins with the preparatory phase: (1) establishing the research questions or hypotheses for the study. (2) The state-of-the-art research methodologies are thoroughly reviewed to test the feasibility of the mixed-methods research design for the proposed study. (3) The study protocol is written and submitted for approval from the ethics committee. Following approval, the issues concerning the clinical trial agreement, informed consent and clinical report forms are dealt with. The patient population is screened for the selection of a sample set of sufficient size, based on specific inclusion and exclusion criteria. Dental, medical and behavioural histories are recorded, complemented with pre-operative radiographic assessment, dental and soft tissue examination. The restorative materials are randomly allotted to teeth subject to restoration, in a ‘split-mouth’ design. The second phase is the restorative phase. (4) A standard cavity preparation protocol with a strict placement technique according to the manufacturer’s instructions is followed by adequate finishing and polishing procedures. All restorations are documented pre- and post-operatively, with and without articulation paper. The third phase is the recall phase. (5) At every recall, a set of wear data is collected from both quantitative and qualitative techniques of wear evaluation, which are carried out simultaneously. (6) The collected qualitative and quantitative data are separately analysed systematically in three steps, namely: data entry, visualisation and statistical analysis. (7) The separately analysed data are compared and consolidated to interpret the laser scan difference images and photomicrographs qualitatively and also to quantitate the marginal degradation observed in the USPHS rating. (8) The interpretations are summarised to either accept or reject the study hypotheses. (9) The research results are reported.



approach presented in this case study is based on ‘between-method triangulation’. This method makes use of qualitative methods (USPHS, SEM) and quantitative (3D laser scan) methods simultaneously and with equal priority.

Collection strategy

At baseline, i.e. after 1 month of clinical service, the investigator gets every patient to brush his or her teeth immediately before the start of the assessment. Subsequently, a brief soft tissue survey is undertaken to ascertain that



7.2 Schematic representation of the sequential procedures of the research study design, exemplifying baseline and 12 months’ recall. Procedures during the restorative phase: (a) pre-operative radiograph of the tooth to be restored; (b) pre-operative clinical photograph of tooth in need of composite restoration (caries or amalgam replacement); (c) cavity preparation; (d) isolated, prepared and finished cavity; (e) post-operative clinical photograph of restored tooth without articulation paper; (f) post-operative clinical photograph of restored tooth with articulation paper. Procedures during the recall phase, i.e. baseline and 12 months recall, are highlighted and the data at 6 months or the long-term 24 and 36 months are not shown. Routine clinical examination including USPHS evaluation, digital mapping and micro-morphologic evaluation are repeated at each recall. Baseline clinical examination: (1a) radiographic assessment of the restored tooth; (1b) baseline clinical photograph of restored tooth without articulating paper; (1c) baseline clinical photograph of restored tooth with articulation marks; (1d) USPHS evaluation for every recall. Baseline digital mapping: (1e) 3D laser scan image of baseline gypsum replica. Baseline micro-morphology evaluation: (1f) complete occlusal surface optical microscopic view of baseline resin replica under $\times 24$ magnification, during optical pre-selection, followed by SEM view; (1g to 1j) quadrant-wise SEM view of the same sample; (1k) SEM photomicrograph of occlusal contact area in enamel (OCAE); (1l) SEM photomicrograph of marginal adaptation; (1m) SEM photomicrograph of occlusal contact area in composite/(OCAC).

The legend of the procedures depicted in the images of baseline recall from (1a) (1j) is not different from the legend of (2a) to (2j) for the 12 months recall phase. In addition, during the digital mapping of the 12 months recall phase, the scanned images of baseline replica (1e) and 12 months replica (2e) are matched to generate difference images (1e2e) in ‘difference modes’. The difference image is subsequently superimposed on the clinical photograph of 12 months (2c) to enable unambiguous interpretation of OCAE, OCAC and degrading margins. Finally, the interpretation made during the clinical examination – including histories and USPHS, digital mapping and micro-morphology evaluation – is extrapolated to provide an explanation for the intraoral bio-tribocorrosion wear behaviour of composites observed in the study.

Table 7.5 Inclusion and exclusion criteria

Inclusion criteria	Exclusion criteria
• Have a need for two posterior tooth-coloured restorations. • A medical history that will not complicate the outcome of the results. • Have a history of brushing his/her teeth at least once a day. • The subject should have a low to moderate caries rate, normal periodontal status with good home care and possess an uncompromised dentition. • Subjects should understand that a minimum of two teeth per subject will be included as part of the study and that an extra restoration could be placed depending on the treatment need. • Subjects who have natural dentition directly opposing the test restoration. Exceptions are made if the opposing dentition is a gold crown. • Only vital teeth with a normal appearance on the radiograph, normal response to palpation, percussion and a favourable response to cold stimulus will be selected. • Patients needing Class I or Class II restorations in posterior teeth: first and/or second mandibular and/or maxillary molars.	• Individuals with a chronic disease with oral manifestations. • Individuals who exhibits gross oral pathology, poor oral hygiene or poor dental health. • Individuals with gross dental caries or severe periodontal problems that could compromise the future of the tooth. • Subjects with allergy to any materials to be used in the study. • Individuals who exhibit signs or symptoms of severe bruxism. • Subjects with porcelain directly opposing the test restoration. • Teeth that will be used as an abutment for removable or fixed partial dentures will be excluded.

there are no soft tissue lesions or pathological conditions. Gingival condition is recorded. Two calibrated investigators, as described by Cvar and Ryge (1971), complete the direct clinical evaluation of restorations with the modified USPHS criteria (Table 7.6). If a parameter is judged to be clinically unacceptable then the exact cause of failure has to be recorded and it has to be decided whether the restoration can be repaired or requires replacement. However, the repaired restorations can still be kept in the study for further recalls. While grading the marginal adaptation, differentiation of cavo-marginal discoloration, recurrent caries and marginal deterioration are elucidated. Intraoral radiographs are taken and post-operative

Table 7.6 Modified USPHS criteria

Category	Rating and characteristics
Anatomical form	A: restoration's contour is continuous with existing anatomical form and margins. B: restoration is slightly over contoured or under contoured. C: marginal overhang or tooth structure (dentine or enamel) is exposed. D: restoration is missing, traumatic occlusion or restoration causes pain in tooth or adjacent tissue.
Secondary caries	A: no visible caries. C: caries contiguous with the margin of the restoration.
Colour match	A: no mismatch in colour, shade or translucency between restoration and adjacent tooth structure. B: mismatch between restoration and tooth structure within the normal range of tooth colour. C: mismatch between restoration and tooth structure outside the normal range of tooth colour. D: aesthetically displeasing colour, shade and translucency.
Retention	A: present. B: partial loss. C: absent.
Marginal adaptation	A: excellent continuity at resin–enamel interface; no ledge formation, no discoloration. B: slight discoloration at resin–enamel interface; ledge at interface. C: moderate discolouration at resin–enamel interface measuring 1 mm or greater. D: Recurrent decay at margin.
Polishability	A: smooth and highly shiny, similar to enamel. B: smooth and satin, highly reflective. C: rough and shiny, satin, somewhat reflective. D: rough and dull or satin, not reflective.
Surface staining	A: absent. C: present.
Sensitivity	Pre-operative sensitivity, Yes/ No. Post-operative sensitivity, Yes/No.
Soft tissue health	A: excellent response – no inflammation. B: slight inflammation of gingival tissue. C: moderate to severe gingival inflammation.
Proximal contact points	A: present. C: absent.

sensitivity, if present, is evaluated by using a cold-based vitality test (e.g. CO₂ snow, Fricar, Odontotest, Zurich, Switzerland) and the sensitivity is scored as positive or negative. An alginate impression is made initially and then a gypsum cast, from which acrylic posterior custom trays are fabricated. The same custom trays are used for impression procedures at each registration session. Each restoration is documented photographically (with and without articulation paper). Impressions of restoration are made at baseline. Two impressions per tooth are taken with polyvinyl siloxane impression material using individualised custom trays. One impression is poured with white stone gypsum GC Fujirock EP White (dental stone type IV, GC Europe, Leuven, Belgium) for laser scanning and another impression with Araldite D, Ciba Geigy (Belgium), for morphological observation complemented with SEM study. All replica models are uniformly trimmed and mounted on aluminium stubs for easy handling and repositioning.

The epoxy replicas are prepared for SEM viewing. Before SEM viewing, the prepared epoxy replicas are subjected to high-magnification dental surgical optical microscopy (OPMI Pro ergo, Carl Zeiss Surgical GmbH, Oberkochen, Germany), in order to downsize the samples for SEM viewing, through pre-selection. The optical microscopy at high magnification ($\times 12$, $\times 24$) has the potential to identify areas of interest – such as OCA, pitting, fatigue cracks, degrading margins and wear steps – for further SEM viewing. Replicas that do not exhibit such characteristic features using the screening optical microscopy view are then eliminated from further SEM viewing, thereby economising on time, effort and cost. The potential samples with interesting ‘hot spots’ are further explored using SEM and quadrant-wide photomicrographs of each sample are made.

The stone replicas are scanned (3D-Laser Pro, Willey Tec, GmbH, Munich, Germany), the recall images digitally subtracted and the total substance loss is determined on the entire filling surfaces as average loss (mean) as well as along the margins on dentine and enamel as maximum depth of the area (0.5% quantile). The wear values are then plotted, representing the absolute wear, referring to baseline condition, as obtained at the recall period.

The data collection strategy is repeated during additional recalls conducted at 6, 12, 24 and 36 months following the baseline recall.

Data analysis

After executing the data collection strategies simultaneously for quantitative and qualitative methods, the wear data must be gathered up for analysis, to see how the data support (or do not support) the study hypotheses. The data analysis task is split into three stages: (1) data entry, (2) visualisation and (3) statistical analysis.

The analysis begins with data entry. Qualitative wear data (USPHS) can make use of Excel's good facilities including simple data forms, data validation and extensive importing facilities. Excel does not impose any discipline, but the subsequent work will be made much easier if data are entered in a structure that Excel calls a 'List'. It is recommended that several worksheets within one workbook can be saved to store data and to protect the entered data from accidental changes by using Excel's 'Protection' facility. Using a statistics software (Statistica Version 7.0, Stat Soft Inc., Oklahoma, USA) package would automatically impose some discipline on the method of data entry that is more appropriate for quantitative wear data (vertical and volume loss). To make the data visualisation facilities easier to use, it is recommended that the dimensionality is reduced for the qualitative data (e.g. percentage calculation for Alpha scores for each criteria at a recall) and quantitative data (e.g. mean and standard deviation of vertical and volume loss for the entire sample size at each recall, differential wear calculation).

Visualisation, involves describing pictorially the qualitative data (e.g. charts, graphs) and quantitative data (e.g. tables, graphs). The graphs are indispensable in discerning the clinical assessment of materials for USPHS criteria, differential wear and wear rate of materials over time. Excel's graphical ('Charting') facilities are generally very good.

Producing graphs from data in worksheets is simple, and the results can easily be modified and tidied up using the extensive and dynamic editing facilities. However, Excel's charts are designed principally for business, and there are some types of graphics needed for exploratory statistical work that are difficult or tedious to produce. For this reason, Statistica can be used to obtain additional types of graph such as box plot, category-value plot and scatter plot. The clinical pictures (pre- and post-treatment, with and without articulation paper), being a part of qualitative data, could be visualised in PowerPoint slides, with all of them arranged in a sequence for every subject. Preparation of patient-specific clinical picture slides renders the interpretation of difference and SEM images much easier and later aids in report submission.

Statistical analysis usually breaks into two parts: (a) descriptive statistics, which summarise the structure and distribution of the data and (b) inference, which forms general conclusions from the observed data. Excel provides a 'Descriptive Statistics' facility as part of the analysis. However, it is rather restricted in scope, as it cannot easily be used to compare statistics of different columns or levels of a factor. Furthermore, the set of statistics it gives is rather limited. For these reasons, the 'Descriptive Statistics' facility of Statistica is recommended for specific statistical tests for one or more columns of data to be described, and/or one or more factors.

Once the data are made more accessible by visualisation and descriptive techniques, formal statistical analysis techniques are needed to identify the data, to investigate the data further and to draw general inferences from them. A very large number of statistical techniques have been developed to handle many different types of data and relationships between them, and it can be difficult and confusing to choose the correct techniques for a given set of data and the requirements of your investigation. Users sometimes drift into statistical inference – which includes standard errors, confidence limits, *t* tests and chi-square tests, etc – without realising where this is leading. In general, it is recommended that advice from a competent statistician be sought for the choice of the most appropriate approach.

With reference to this case study, statistical analysis can be performed with Statistica for the clinical USPHS data and the wear quantification data. Statistica supports many of the standard statistical methods, is generally easy to use and is reliable. The sign test can provide the comparative statistical analysis of the materials over the study period. For each evaluated USPHS criteria of each material group, further analysis can be done using the Friedman analysis of variance (ANOVA) (by ranks) and Kendall Concordance test for changes from baseline to 6, 12, 24 and 36 month data. The McNemar test can assess the statistical significance of the changes in lower ranking criteria. The level of significance needs to be set at $P \leq 0.05$ for all tests. In addition to ranking, the vertical loss, volume loss and differential wear rates of materials are compared with those of referenced enamel for inferring the statistical significance for the observed differences in rating the clinical wear performance as acceptable or unacceptable.

Interpretation

Owing to the mixed-method research approach, the qualitative and quantitative wear data need to be correlated and consolidated for effective interpretation of data relating back to the research hypotheses of the study. Data correlation involves the quantitative data being compared and correlated with the qualitisied data or the qualitative data being correlated with the quantitised data. This is followed by data consolidation, wherein both quantitative and qualitative data are combined to create new or consolidated variables for further interpretation. One can design a correlation–consolidation strategy as illustrated in Table 7.7. However, the researcher can use study-specific strategies and not be limited by this example.

Although the strategy displayed in Table 7.7 overstates the significance of clinical photos, the importance of other sorts of data is not to be underestimated. For example, the clinical photos aid in collating the material loss at the restoration peripheries, seen in the difference image and SEM

Table 7.7 Wear data correlation and consolidation

Parameters	Correlation	Consolidation
Wear	Clinical photos – with contact points, patient histories, difference image, vertical loss values, volume loss values	OCAE wear – heavy, light OCAC wear Wear steps
Fatigue	Clinical photos – with contact points, difference image, SEM photomicrographs	Pitting Plucking Cracks
Restoration periphery	Clinical photos – with contact points, patient histories, difference image, vertical loss values, SEM photomicrographs	Degrading margins Chipping of excess material at margins

photomicrographs, as degrading margins or disappearance of excess material at margins. However, this collation can only be achieved after manually superimposing the difference image over the clinical picture of the restoration. Nevertheless, it is almost impossible to appreciate clinical material loss at margins until the cavo-surface angle is exposed as much as 150–175 μm , and, in such cases, the clinical photos do not stand alone, as other measures will show these defects.

The addition of qualitative (USPHS ratings, patient histories, SEM photographs) and quantitative data (vertical loss in micrometres, volume loss in cubic millimetres, magnitude of degrading margins) during interpretation, helps to decipher the multi-factorial nature of intraoral wear tribology or bio-tribocorrosion. For instance, a patient's complaint, as recorded during their history-taking, of catching the margins of a restoration with fingernails, may be sufficient evidence to interpret the colour gradients along the restoration's margin and the micro-gap observed in SEM photomicrograph, as marginal degradation. A correct behavioural history might attribute the increased volume loss of posterior composite restorations to bruxism, dietary habits and the type of articulation.

Drawing conclusions

Drawing valid conclusions involves summarising the interpretations with supportive evidences and making judgments that will withstand scrutiny.

Based on the judgements, the null hypothesis (Table 7.4) is either accepted or rejected.

Writing a final report

A clinical study report is prepared as a key document, accurately and completely reporting all relevant information arising from the investigation. Investigators should make use of the CONSORT statement (Moher *et al.*, 2001) in reporting (a) the research study design and (b) the operational procedures of the study. Slide presentations of the photo documentation in a sequential manner such as pre-operative status of the tooth, stages of cavity preparation, restoration and finishing, followed by the clinical photos with and without the OCA registration with occlusal foil, help the reader to appraise the study design and reproducibility. All failures have to be reported, including the causes and the operational details of repair or replacement undertaken in such cases. Statistical analysis including randomisation, choice of statistical tests and failure analysis deserve detailed documentation.

The research study design presented in this case study has been framed carefully to guide researchers interested in implementing mixed-methods approach in a randomised controlled clinical trial to investigate wear. Although the case study exclusively focuses on wear investigation in posterior composite restorations, the presented study design can be generalised to any randomised controlled clinical trial investigating the clinical performance of dental restorative materials. Table 7.8 presents the features in mixed-methods study design that overcome the existing shortcomings in clinical research study design, as reported by Hickel *et al.* (2007). It is worth mentioning that the features are already in compliance with the recent recommendations published by Hickel *et al.*, (2007) for conducting controlled clinical studies of dental restorative materials to overcome the reported shortcomings.

7.6 Future trends

The mixed-methods approach in wear research is an attempt to legitimise the use of multiple methods in evaluating wear of materials, rather than restricting or constraining researchers' choices. It is an expansive and creative form of research, not a limiting form of research. It is now time that researchers formally recognise this third research paradigm and begin using it systematically. In general, we accept that quantitative, qualitative and mixed research are all superior under different circumstances and it is the researcher's task to examine the specific contingencies and make the

Table 7.8 Reported shortcomings versus features in mixed-methods study designs

Reported shortcomings in clinical study design	Features in mixed-methods research study design that overcome the shortcomings
• Incomplete reporting of results. • Inappropriate statistical analysis. • Inability to reproduce. • Non-evidence-based evaluation criteria. • Inadequately considered patient factors. • Insufficient reporting on operational procedures. • Over-estimated secondary caries scores • No evidence-based acceptance level for marginal deterioration • Uncontrolled confounding variables and bias	• Report preparation through the use of CONSORT statement, slide preparation. • Statistical analysis considers each subject as a single statistical unit, with dependence between the different restorations. • Detailed documentation of study design, operational and analysis procedures permitting reproducibility. • USPHS system of grading is evidenced qualitatively with SEM and qualitatively by 3D laser scanning. • Recording patient history focuses on patient factors. • Slide presentation of the photo documentation of operational procedures. • Careful discrimination of cavo-marginal discolouration and secondary caries. • USPHS scores for marginal adaptation are correlated qualitatively with SEM and quantitatively with measured marginal gap in 3D laser scan. • Employing different operator and evaluator, randomisation and predefined inclusion and exclusion criteria.

decision about which research approach, or which combination of approaches, should be used in a specific study. In this chapter, we have outlined some of the common wear research methodologies, we have described the concept of mixed-methods research, provided a specific triangulation model, and provided tables of quantitative and qualitative wear research strengths and weaknesses to help apply the principle. In addition, we have provided a mixed-methods case study design in compliance with the recently published recommendations for conducting controlled clinical studies of dental restorative materials, in order to promote the use of this approach in wear research. We hope we have made the case that the mixed-methods approach is here to stay and that it should be widely recognised in wear research as the third major research paradigm that has the potential to reduce some of the problems associated with singular methods. By utilising quantitative and qualitative techniques within the same framework, mixed-methods research can incorporate the strengths of both methodologies. Most importantly, investigators who conduct mixed-methods

research are more likely to select methods and approaches with respect to their underlying research questions, rather than with regard to some pre-conceived biases about which research paradigm should have domination in wear research. By narrowing the divide between quantitative and qualitative researchers, mixed-methods wear research has a great potential to promote a shared responsibility in clinically appraising the technical excellence of restorative materials, in the context of the oral environment. The time has come for mixed-methods research to explore the intraoral wear tribology of posterior composites.

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8.1 Introduction

8.1.1 Failure of restored teeth

Although the rapid developments in dental biomaterials and bonding techniques have significantly improved their mechanical performance, failures of dental restorations still occur. A retrospective clinical study on the longevity of posterior restorations indicates that about 8% and 18% of resin composite restorations fail at 5 years and 10 years, respectively.¹ The corresponding figures for amalgam restorations are 10% and 21%.¹

There are many factors that cause failure of dental restorations, with secondary caries and fracture of teeth or restorations cited as the most important.^{1,2} Caries was found to be more common in composite restorations, while fracture of the tooth was more common in amalgam restorations. This was attributed to the fact that amalgam restorations are not adhesively bonded to the cusps, causing them to be more susceptible to crack initiation and propagation from the highly stressed internal line angles.¹

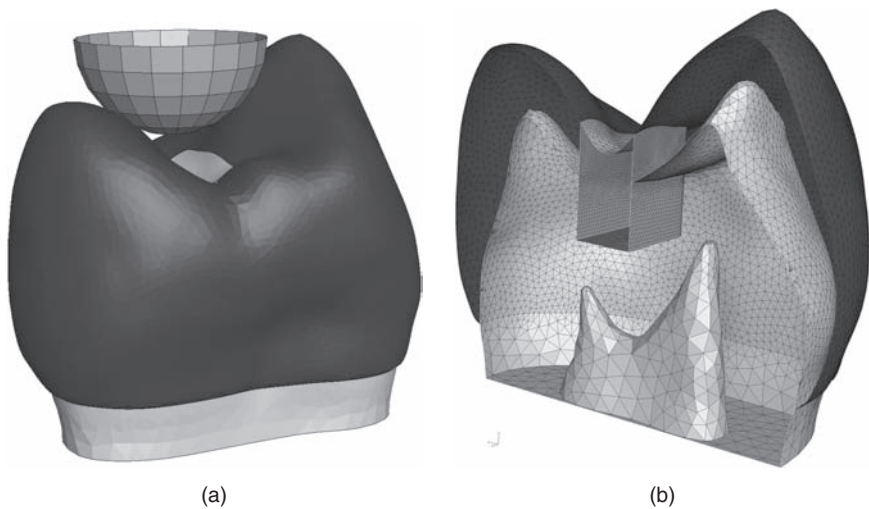
Secondary caries occurs at the margin of an existing restoration. In amalgam restorations, marginal fracture is considered as a precursor to secondary caries.³ Even in the absence of secondary caries, marginal fracture may still lead to premature replacement of the restoration.⁴ For composite restorations, an analysis of the findings of a multi-centre clinical trial revealed that restorations with marginal deterioration at year 3 were more likely to have failed by year 5 than restorations without marginal deterioration at year 3.⁵ There are many reasons for marginal deterioration. Experiments have shown that both occlusal load cycling and shrinkage of the composite material undermine marginal integrity,^{6,7} with the stresses produced by occlusal loading and polymerisation shrinkage causing failure at the tooth–restoration interface.

An ideal cavity shape should minimize stress concentrations along the tooth–restoration interface due to sharp angles or differences in material

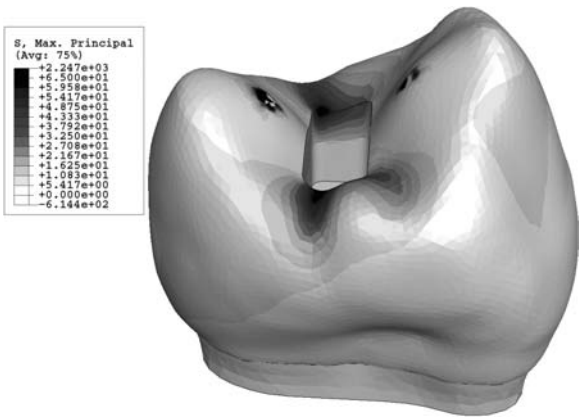
properties. If the stresses along the interface can be kept lower than the mechanical strength of the bond, marginal deterioration in a composite restoration can be reduced, thus prolonging the lifetime of the restoration. Moreover, a lower stress level along the interface, with or without bonding, could also reduce the likelihood of fracture of both the restoration and tooth.¹ Some cavity shapes were proposed by Porte *et al.*⁸ in an experiment to investigate shrinkage stresses. Cavities with large cavo-surface angles, which led to low stress concentrations near the free surface, resulted in better marginal integrity. A subsequent finite element (FE) study confirmed these findings.⁹

Figure 8.1 shows the FE model for the crown of a premolar tooth with a Class-I composite restoration. The geometry and dimensions of the model may be derived from computed tomography (CT) scan images of a real restored tooth. Occlusal loading is applied through a rigid hemisphere in contact with the cusps.

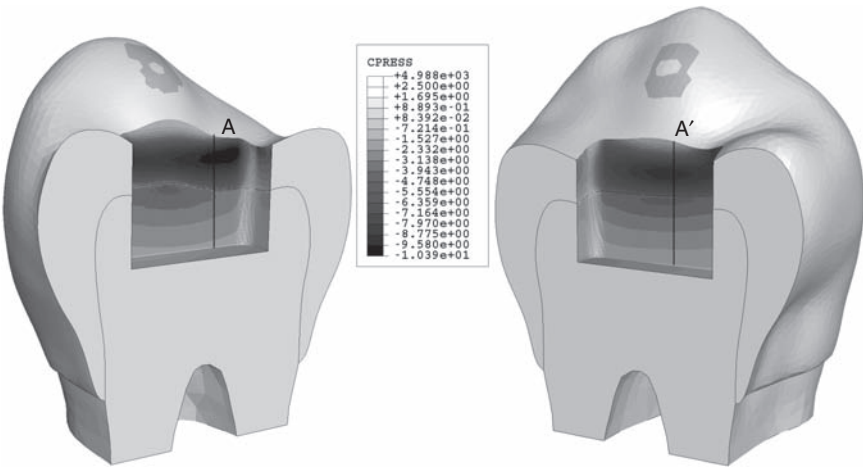
Figure 8.2 shows contours of the maximum principal stresses within the tooth. The restoration has been removed from the figure to show the stresses inside the cavity. Ignoring the contact stresses induced by the rigid hemisphere, the highest tensile stresses (darker grey) are located at the mesio-distal aspects of the restoration margin on the occlusal surface. These stress concentrations may lead to marginal deterioration of the restoration as well as crack initiation in the enamel.



8.1 FE model of a tooth with a Class-I restoration: *a* overall geometry, *b* details of mesh.



8.2 Maximum principal stress contours (MPa) in the restored tooth (restoration removed to show stresses within the cavity).



8.3 Normal stresses (MPa) at the tooth–composite interface. CPRESS, contact pressure, which is equivalent to the normal stresses in this case.

Figure 8.3 shows contours of the interfacial stresses normal to the tooth–composite interface. The tooth, with its restoration removed for clarity, is split mesio-distally into two approximately equal halves to reveal stress distributions on the cavity surfaces. As shown in this figure, very high tensile stresses (darker grey) exist in the enamel region on the buccal and lingual surfaces of the cavity, which can result in debonding of the restoration from the tooth.

Attempts at applying shape optimization techniques to the design of dental restorations have been made by Proos *et al.*¹⁰ and Guillaume *et al.*¹¹ They optimized the designs of ceramic dental bridges and cavity shapes respectively, using nature-inspired structural optimization methods to minimize stresses in the restorations under occlusal loading. The work by Guillaume *et al.*¹¹ considered standard cavity shapes with weakened tooth–restoration bonding and the modifications introduced were mainly to the internal line angles only. This chapter describes how shape optimization techniques may be used to derive alternative cavity shapes to minimize the interfacial stresses for bonded restorations under occlusal loads.

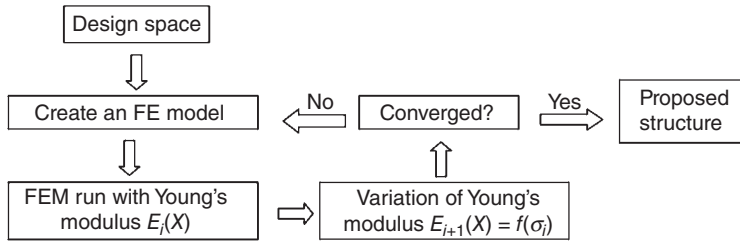
8.2 Methods

8.2.1 Shape optimization based on the principle of adaptive growth

Biological structures are able to adapt their growth to external mechanical stimuli and impacts. For example, when plants are under external loads, such as wind force and self-weight, the overloaded zones are reinforced by local growth acceleration and the unloaded zones stop growing or even shrink. Such phenomena are recorded in the annual rings of trees. Through his observation of the stems of spruce, K. Metzger, a German forester and author, realized that the final goal of the adaptive growth exhibited by biological structures over time is to achieve uniform stress distribution within them. He published his discovery in 1893.¹² A team of scientists at Karlsruhe Research Centre adopted Metzger’s observations and developed them to one single design rule: the axiom of uniform stress. The methods derived from this rule are simple and brutally successful like nature itself. An excellent account of the uniform-stress axiom and the optimization methods derived from it is given by Claus Mattheck in his book ‘*Design in Nature*’.¹³ The present study utilizes one of these methods, stress-induced material transformation (SMT), to optimize the cavity shape of dental restorations.

8.2.2 Stress-induced material transformation (SMT)

As one of the simplest structural topology optimization methods, SMT can be achieved computationally using the FE method, as illustrated in Fig. 8.4. Firstly, the design space is filled with a material of a uniform Young’s modulus E and the corresponding FE model under the anticipated loading condition is analysed to obtain the stress distribution in the structure. Next, the local E value is modified according to the stresses calculated in the previous step using a predefined function ($E = f(\sigma)$). For example, E can be set to be proportional to the von Mises stress. In this way, more heavily



8.4 Flow diagram of the SMT optimization method. FEM, finite element method; E_i , Young's modulus at the i th iteration; σ , the von Mises stress; $f(\sigma)$, a predefined function of σ .

loaded zones are strengthened and the lightly loaded zones are softened, which is analogous to the deposition and resorption processes in living bone. After that, the new and inhomogeneous structure is subjected to the same loading condition and the process is repeated again and again until a converged state is achieved, i.e. the material is iteratively redistributed within the design space. The resulting material layout provides the optimal starting point for the design.

The key in this first stage of the optimization process is the function $E = f(\sigma)$, which could affect both the results and the efficiency of the process. Several functions have been proposed. The simplest one used by Mattheck¹³ is the one-to-one function ($E = \sigma$), but it has low efficiency. Moreover, structures derived using this function have a wide range of Young's modulus values, making them difficult to manufacture. A better function, also proposed by Mattheck,¹³ uses the stress-increment-controlled method. With this method, the Young's modulus of an element is changed according to:

$$E_{i+1} = E_i + k(\sigma_i - \sigma_{\text{ref}}) \quad [8.1]$$

where E_i and σ_i are Young's modulus and stress at the i th increment, respectively; σ_{ref} is a reference or threshold stress above which changes to Young's modulus will occur; and k is a parameter that controls the rate of change of Young's modulus. The stress-increment-controlled method has high efficiency and can be used to adjust the volume of the structure being optimized by choosing different values of σ_{ref} . However, the structure thus created still has a wide distribution of Young's modulus values. To avoid this problem, equations [8.2] and [8.3] below were added to constrain the change of Young's modulus:

$$E_{i+1} = E_1 \quad \text{if } E_{i+1} < E_1 \quad [8.2]$$

$$E_{i+1} = E_2 \quad \text{if } E_{i+1} > E_2 \quad [8.3]$$

E_1 and E_2 are, respectively, the maximum and minimum values of Young's modulus allowed in the structure. The functions [8.1], [8.2] and [8.3] dictate that there can only be two materials in the structure throughout the optimization process. For example, when dealing with cavity optimization, E_1 is the Young's modulus of the tooth tissue, either enamel or dentine, depending on the region of the structure concerned. E_2 is the Young's modulus of the composite. The reference stress σ_{ref} is the failure stress of the interfacial bond.

A user material subroutine (UMAT) in ABAQUS¹⁴ was created to implement the SMT method within the commercial FE program. The UMAT contains a constitutive material model which is able to change its properties according to the stresses as described above. The program is used iteratively during the FE analysis until the spatial distribution of Young's Modulus converges.

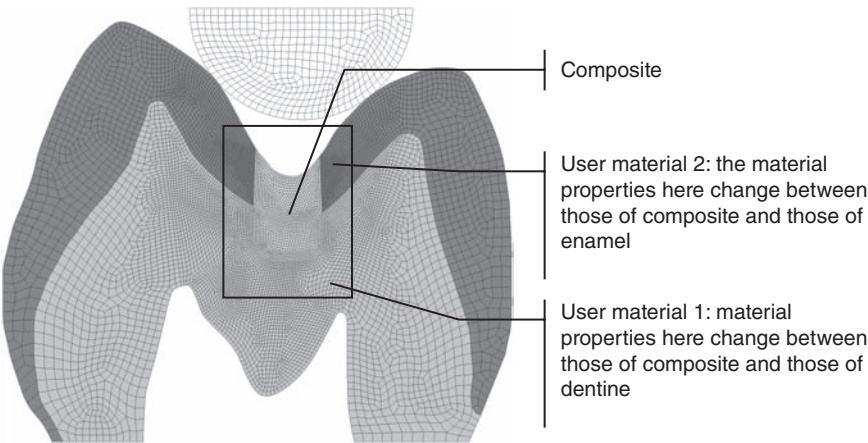
8.3 Application

8.3.1 Shape optimization of cavity shape using stress-induced material transformation

The SMT method is applied to tooth tissues, both enamel and dentine, around the tooth–restoration interface in a restored tooth with a conventional Class-I cavity design. Bonding at the interface is assumed to be perfect. The objective of the exercise is to improve the conventional cavity shape by finding an alternative design with a more favourable interfacial stress distribution under occlusal loading.

The two-dimensional FE model used for deriving the optimized cavity design is shown in Fig. 8.5. Three-dimensional models were not used because the computational effort required would be prohibitively expensive. Nevertheless, a very fine mesh, with an average element length of 0.04 mm in the area of interest, is employed in the two-dimensional model to ensure the accuracy of the solutions. Two user materials (UMAT) are defined, one for the enamel ($E_{\text{enamel}} = 80 \text{ GPa}$) region and the other for the dentine ($E_{\text{dentine}} = 20 \text{ GPa}$) region, as shown in Fig. 8.5. The Young's modulus of an element at the tooth–restoration interface is changed from that of dentine or enamel to that of the restorative material if the local interfacial stress exceeds the reference stress, which is taken to be the microtensile bond strength. The tooth–restoration interface gradually shifts in space until all the interfacial stresses fall below the reference stress. In order to limit the size of the problem, only elements within the rectangular box in Fig. 8.5 are subjected to property changes.

The material properties of enamel, dentine and composite are assumed to be isotropic and linearly elastic; their values are shown in Table 8.1.^{15–18}



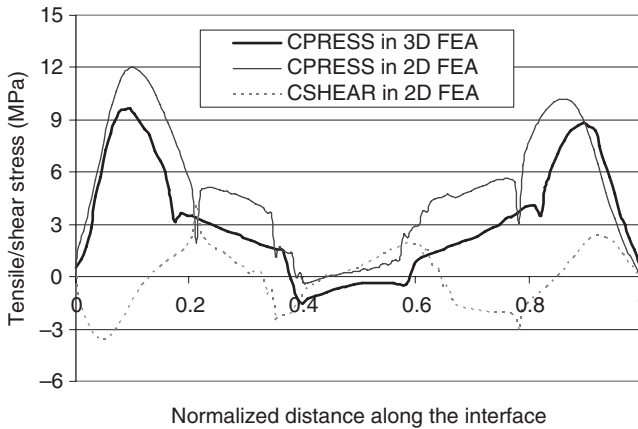
8.5 The FE model with conventional cavity design to be optimized using SMT.

Table 8.1 Restoration and tooth material properties

	Young's modulus	Poisson's ratio
Composite	19 GPa	0.24
Enamel	80 Gpa	0.30
Dentine	20 Gpa	0.31
Pulp	2.07 MPa	0.45

Since the pulp is much softer than enamel, dentine or composite (see Table 8.1), it is excluded from the FE model. Perfect bonding is assumed between the tooth and the composite restoration. The model is fully constrained at the lower boundary close to the enamel–dentine junction. A rigid ball with a diameter of 4.7mm is used to apply occlusal loading to the tooth.

The reference stress, σ_{ref} , is chosen to be the strength of the bond between tooth tissue and restoration, on the assumption that debonding of the restoration is the more frequent failure mode. Much work has been done to determine such bond strengths.^{19,20} However, depending on the type of adhesive, method of surface preparation and test procedure, a wide range of values have been reported.²¹ In this chapter, the tensile strengths of bonds created using RelyX Unicem (3M ESPE),¹⁹ 19.6MPa for enamel restoration and 15.9MPa for dentine restoration, are chosen to be the basic reference stresses. Assuming that the bond strength would deteriorate over



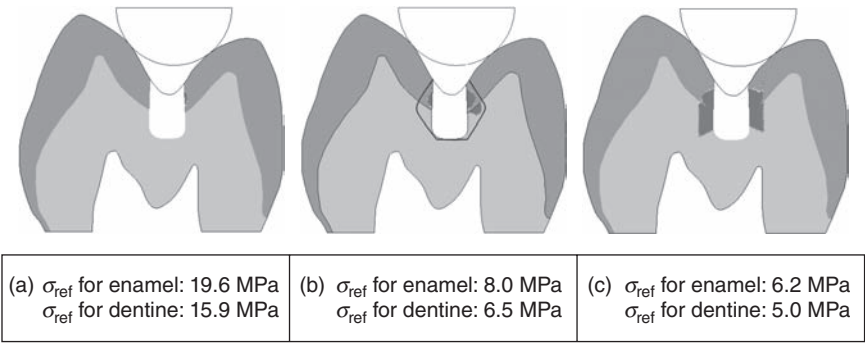
8.6 Interfacial stress distributions along the tooth–restoration interface for a tooth with a Class-I restoration of conventional cavity design.

time, two other sets of reference stresses, which are lower than the original values, are also considered.

The normal stresses, which are mostly tensile, along the tooth–restoration interface before shape optimization are plotted in Fig. 8.6. The results from the three-dimensional model (i.e. along the path AA' in Fig. 8.3, which covers both the buccal and lingual cavity walls and the dentinal floor) are also plotted in Fig. 8.6 for comparison. As can be seen, the two sets of results are very similar, which indicates that the two-dimensional model is representative and justifies its use in the optimization work. Figure 8.6 confirms that the most vulnerable areas in terms of debonding are within the enamel–composite interface. Under an occlusal load of 200 N, the maximum tensile interfacial stress is about 10–12 MPa. Such high stress concentrations may cause marginal deterioration or even fracture of the tooth.

8.3.2 Results from shape optimization

The results from using SMT to optimize the cavity shape are shown in Fig. 8.7 in the form of Young's modulus distribution. The regions where material transformation has taken place are indicated in darker shades of grey. Using the first set of bond strengths as the reference stresses and an occlusal load of 200 N results only in a very small change to the enamel region (Fig. 8.7a). When the reference stresses for enamel and dentine are reduced to 8.0 and 6.5 MPa, respectively, more enamel and dentine are transformed to composite, giving a more extended cavity space (Fig. 8.7(b)). Further reduction of the reference stresses, to 6.2 MPa and 5.0 MPa, leads to an even larger cavity. In this case, however, the cavity reaches the boundary



8.7 Cavity shape optimization using SMT with various reference stresses. Regions where material transformation has taken place are shown in darker shades of grey. Occlusal load, 200 N.

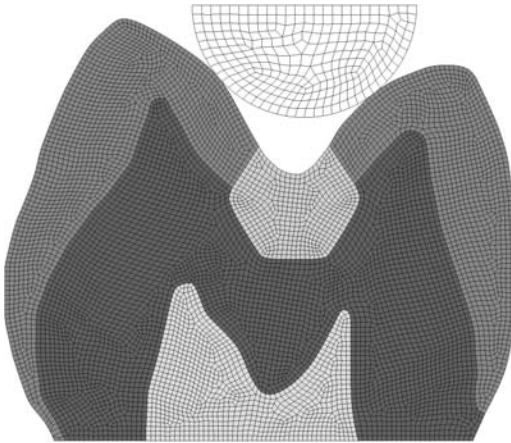
set for SMT (Fig. 8.7c), which means that the area of interest needs to be extended if convergence is to be obtained.

The above results indicate that, under perfect bonding conditions, the optimal cavity should have a wider cavo-surface opening in order to minimize the interfacial stresses under occlusal loads. It is interesting to note that the resulting cavity shape, especially the one indicated in Fig. 8.7(b), is rather similar to the curved bevel joint proposed by Hembree and Andrews in their study on the effect of cavo-surface designs on microleakage in composite restorations.²² The results also show that there are no material changes at the floor of the cavity, which suggests that a deeper cavity is not required.

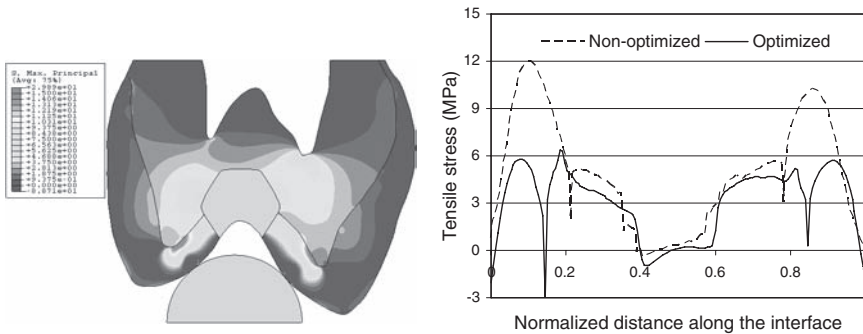
An improved cavity shape may then be drawn up based on the SMT results for the second set of reference stresses/bond strengths; see Fig. 8.7(b). The width of the cavity is increased where the stresses are highest, while the depth is kept the same as in the original design. The new cavity thus has the approximate shape of a hexagon, with the cavo-surface angle being $\sim 90^\circ$. Further FE analysis (Fig. 8.8) is then performed to verify the interfacial stresses in the new design.

8.3.3 Verification of the optimized design

Figure 8.9 shows the maximum principal stress contours and the corresponding stress distribution along the tooth–restoration interface. Compared with the stresses in the original design (Fig. 8.6), the two stress peaks at the enamel–composite interfaces are reduced from 12 to 6 MPa, lower than the reference stress of 8 MPa for enamel. Although the maximum stress at the dentine–composite interface is increased slightly, it is still lower



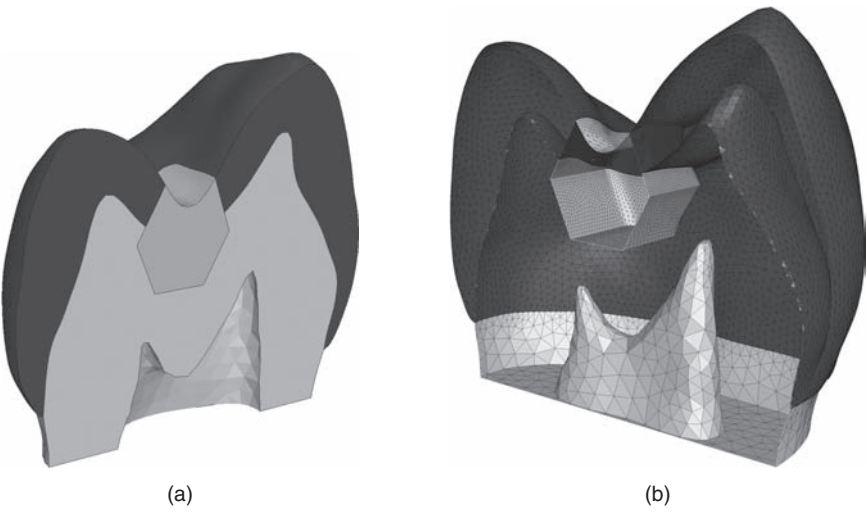
8.8 FE model of restored tooth with the optimized cavity design.



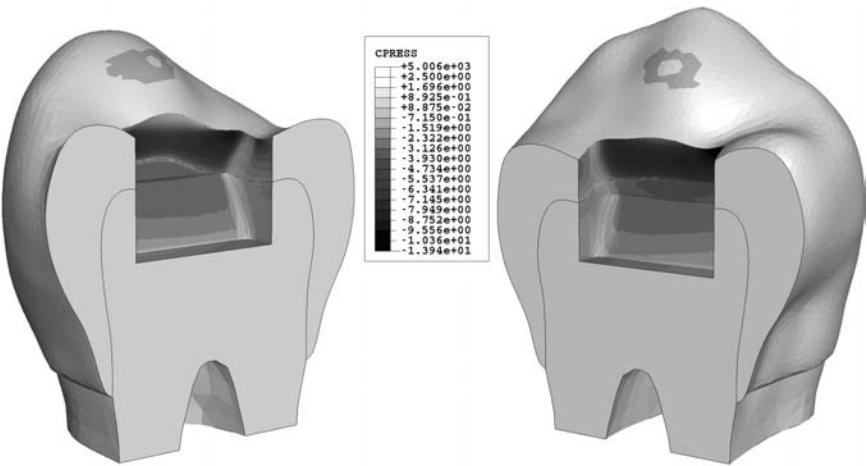
8.9 Maximum principal stress contours (MPa) and stresses along the tooth–restoration interface for the SMT optimized cavity design with perfect bonding.

than the reference stress for dentine (6.5 MPa). The FE analysis results, therefore, confirm that the new design would reduce the interfacial stresses between the composite restoration and tooth tissues due to occlusal loading and, thus, could potentially prolong the lifetime of the restoration.

Strictly speaking, the two-dimensional models are more relevant to a tooth with a mesial–occlusal–distal (MOD) restoration, since the cavity shape is assumed to be uniform over the thickness. It would be useful to see whether the newly proposed cavity shape could actually reduce the interfacial stresses in the more confined Class-I restoration. A three-dimensional FE model can, therefore, be created for the restored tooth with the optimized cavity design. The model and its internal mesh density are shown



8.10 Three-dimensional FE model of restored tooth with the optimized cavity design.



8.11 Contours of normal stresses (MPa) at the tooth–composite interface of the optimized cavity design.

in Fig. 8.10. Contours of the normal stresses along the tooth–restoration interface are shown in Fig. 8.11, which has the same grey-scale spectrum for stresses as that in Fig. 8.3 to allow direct comparison. Compared with those in the original cavity design, the interfacial stresses in most areas can be seen to be reduced significantly. However, stress concentrations still exist at some of the sharper corners of the restoration margin.

8.4 Summary

Shape optimization techniques are used successfully to derive cavity shapes with lower interfacial stresses under occlusal loading. The optimized cavity shapes can therefore potentially prolong the life of restorations and reduce the incidence of fracture in restored teeth. Although only Class-I restorations are considered here, the techniques can be applied to other cavity shapes as well as other types of restoration such as dental implants. Also, the work can be extended to cover shrinkage stresses induced by polymerization of composite restorations.

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Fibre-reinforced composites for dental applications

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9.1 Introduction

A new group of non-metallic dental biomaterials that are increasingly being used in dental applications are fibre-reinforced composites (FRCs). These materials were originally developed as part of a reinforcing system for denture bases in the early 1960s.¹ In principle, the FRCs could have been developed as tough tooth-coloured materials at the time of the introduction of Bowen's resin (in 1962). Clearly, this did not happen because there were problems in combining resin systems with reinforcing fibres, resulting in difficult handling of the FRC both clinically and technically. Development of the FRCs with new types of resin systems along with a better understanding of the design principles behind the construction of fibre-reinforced devices, has led to the use of FRCs in a variety of disciplines and applications: in removable prosthodontics,^{2–7} fixed prosthodontics,^{7–26} restorative dentistry,^{27–30} periodontology,^{31,32} and orthodontics^{33,34} and in repairs of fractured porcelain veneers.^{35,36} Critical evaluation of the available FRC materials and recommendations for patient selection are of great importance for successful outcomes.

9.2 Structure and properties of fibre-reinforced composites

FRC is a material combination of polymer matrix and reinforcing fibres. Fibres of the composite act as the reinforcing phase when the load is applied to the composite.³⁷ Load is transferred to – and carried by – the fibres. The reinforcing fibres can take the form of continuous unidirectional (rovings), continuous bidirectional (weaves) or continuous random-oriented (mat) configurations, or short random-oriented fibres.

Of the many types of fibre that are available, the most clinically suitable have proved to be glass fibres which can be silanised and bonded to the resin matrix of the FRC.^{38–40} Glass fibres vary according to their

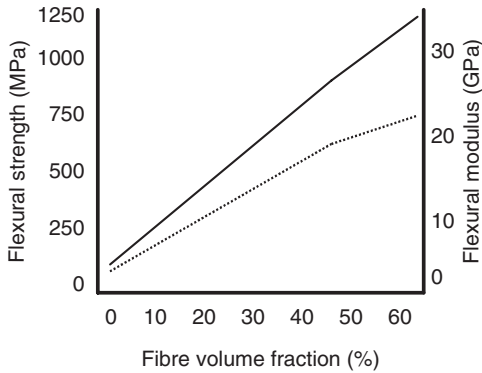
Table 9.1 Factors contributing to the physical properties of FRCs

Properties of fibres versus properties of matrix polymer
Impregnation of fibres with resin
Adhesion of fibres to matrix
Quantity of fibres
Direction (orientation) of fibres
Location and volume fraction of fibres in construction

composition and the most commonly used fibre is E-glass (electrical glass) which offers chemically stable and durable glass in the pH range of 4–11.⁴¹ Other fibres that have been used have included carbon/graphite fibres, but their black appearance limited their clinical use.⁴² Attempts to use ultra-high molecular-weight polyethylene (UHMWP) fibres have also been made^{3–7,43–46} but there are problems in bonding these fibres to the resin matrix.^{47,48} In addition, oral microbes have a high affinity for this material, adhering to the UHMWP FRC; this may limit their use as a dental material, as concluded by Tanner *et al.*^{49–51} and Vallittu.⁵² Obviously, the strength and rigidity of a specific construction made from FRC is dependent on the polymer matrix of the FRC and the type of fibre reinforcement. The factors influencing the properties of FRCs are listed in Table 9.1.

In dental appliances of relatively small size, the quality of the load-bearing FRC substructure is of importance. From this perspective, all of the aforementioned factors that influence the properties of FRCs must be carefully taken into consideration. This is especially important because mastication causes dental appliances to be subjected to patterns of cyclic loading. Therefore, not only should the appliance have adequate static strength, but also adequate dynamic (fatigue) strength. It should also be noted that dental constructions are multiphase in nature, e.g. FRC-reinforced root-canal-post systems consist of dentine, resin composite cement, core build-up resin composite, and, as a load-bearing component there is the FRC root canal post. All of these materials need to have adequate strength and adhesive compatibility. By increasing the fibre quantity in the resin matrix, the strength of the FRC and the flexural modulus are increased (Fig. 9.1).

An important parameter responsible for the strength of the FRC is the impregnation of the fibres with resin. Reinforcing fibres are difficult to impregnate with resin systems of high viscosity.^{52–54} Such highly viscous resin systems are, in particular: those mixed from polymer powder and monomer liquid which are used in denture bases, provisional fixed partial dentures (FPDs), and removable orthodontic appliances; or those made of light-curing resins and particulate fillers. A manufacturer-applied resin impregna-



9.1 Ultimate flexural strength and modulus of elasticity of unidirectional FRC plotted against the E-glass fibre volume fraction (solid line, flexural strength; dashed line, flexural modulus) (three-point bending test, span 10 mm).

tion of fibres used in dentistry is recommended to ensure complete impregnation of the fibres by the resin.⁵⁵ The complete impregnation of fibres by the resin allows the resin to come into contact with every fibre. If complete impregnation is not reached due to high resin viscosity, or polymerisation shrinkage of the resin, then the mechanical properties of the FRC will not reach the optimal values calculated from the laws of mixture.⁵⁴

Two types of resins, resulting from a cross-linked (thermoset) or linear (thermoplastic) polymer matrix can be used in FRCs. A cross-linked matrix is formed from multifunctional or dimethacrylate resins, whereas monofunctional methacrylates form a linear (non-cross-linked) polymer matrix. There are also impregnation methods based on using combinations of thermoset- and thermoplastic-type resins. The polymer matrix is multiphase in nature, and it is, by definition a semi-interpenetrating polymer network (semi-IPN) having the cross-linked polymer and the linear polymer mixed together.^{56–58} In polymerisation the dimethacrylate monomers form a predominantly cross-linked semi-IPN structure with phases of the linear polymer polymethyl methacrylate (PMMA). A cross-linked polymer matrix forms a stiffer FRC than that obtained by thermoplastic or semi-IPN polymers.^{59–61} On the other hand, thermoplastic and semi-IPN polymer matrices provide higher toughness than FRCs made of highly cross-linked thermosets. The semi-IPN polymer matrix of a FRC provides benefits over cross-linked dimethacrylate or epoxy polymer-type matrices in both handling properties and the bonding of indirectly made restorations and root canal posts to resin luting cements and veneering composites.^{27,57,62} Table 9.2 lists currently available resin-impregnated or pre-impregnated dental FRC

Table 9.2 Resin-impregnated dental FRC products classified according to the resin matrix and fiber type

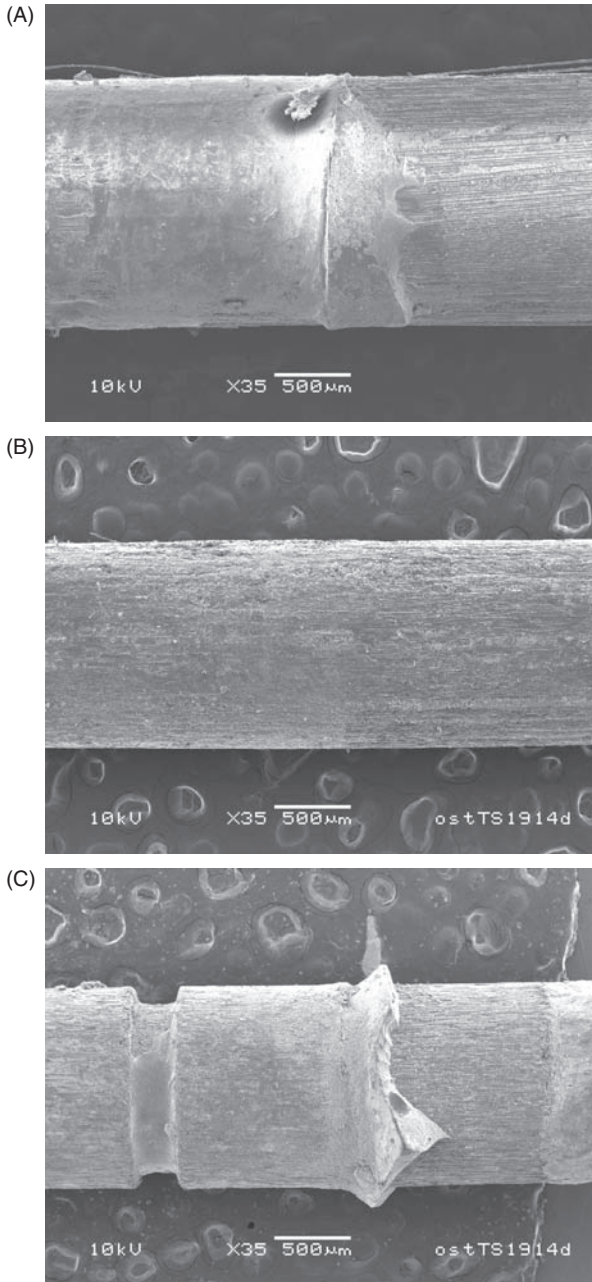
Brand	Manufacturer	Fibre	Resin
Vectris	Ivoclar-Vivadent, Liechtenstein	Glass (continuous unidirectional and bidirectional)	BisGMA TEGDMA
FibreKor	Jeneric-Pentron, USA	Glass (continuous unidirectional)	BisGMA
Splint-It	Jeneric-Pentron, USA	Glass (continuous unidirectional)	BisGMA
Stick, StickNet	Stick Tech, Finland	Glass (continuous unidirectional and bidirectional)	PMMA**
everStick, everStickNet	Stick Tech, Finland	Glass (continuous unidirectional and bidirectional)	Semi-IPN of BisGMA-PMMA
everStick POST PERIO ORTHO EG Fibres	Stick Tech, Finland Kuraray, Japan	Glass (continuous unidirectional) Glass (continuous unidirectional)	Semi-IPN of BisGMA-PMMA UDMA
Dentapreg Splint, Retainer, Bridge	Advanced Dental Materials, Czech Republic	Glass (continuous unidirectional)	BisGMA
FibreX-Lab	Angelus Dental Solutions, Brazil	Glass (continuous unidirectional)	BisGMA-UDMA

* Abbreviations: TEGDMA, triethylene glycol dimethacrylate; BisGMA, bisglycidyl-A dimethacrylate; PMMA, polymethyl methacrylate, ** requires further manual impregnation before use; UDMA, urethane dimethacrylate.

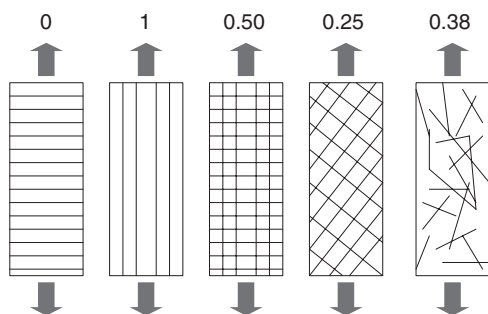
products. Figure 9.2 shows the bonding of resin composite luting cement to root canal posts with a cross-linked or semi-IPN resin matrix.

9.2.1 Mechanical strength

The highest static strength (ultimate flexural strength) of the FRC requires a fibre density of approximately 70 vol% (Fig. 9.2). A high-quality glass FRC material with high fibre density provides high flexural properties (with E-glass at 1250 MPa) (Fig. 9.1).^{59,60} Water sorption of the polymer matrix reduces the strength and modulus of elasticity of the FRC of semi-IPN polymer matrix by approximately 15% within 30 days of water storage at 37 °C.⁶² A positive correlation exists between water sorption of the polymer matrix and the reduction of flexural properties.⁶⁰ For instance, high water sorption of a polyamide (nylon) matrix causes a reduction of over 50% in



9.2 Scanning electron micrograph of the surface of an FRC root canal post after being pushed out from the composite resin luting cement. Post with (A) semi-IPN polymer matrix and (B and C) cross-linked matrix with or without serrated surface. Note good bonding of cement to semi-IPN post by secondary IPN bonding mechanism. (Courtesy of Dr Anna-Maria Le Bell and Quintessence Publishing.)

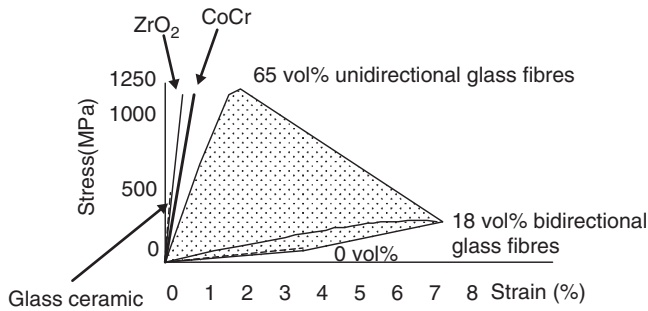


9.3 Reinforcing efficiency (Krenchel's factor) of fibres with different fibre orientations in plane.

the strength of a FRC. The reduction of the flexural properties is reversible, i.e. recovery of the mechanical properties of the FRC occurs following dehydration.⁶⁰ In another study, no significant reductions of flexural strength and modulus were evident even after long-term water storage (up to 10 years).^{63,64}

The strength of an FRC is also dependent on the fibre direction. The efficiency of the fibre reinforcement (Krenchel's factor) varies in FRC laminates with different fibre orientations (Fig. 9.3).⁶⁵ The continuous unidirectional fibres give the highest strength and modulus of elasticity for the FRC but the property is available only when the direction of stress is the same as that of the direction of the fibres. Anisotropic behaviour of unidirectional FRCs can also be seen in other properties, such as thermal expansion or polymerisation shrinkage.⁶⁶ The reinforcing effect of fibres can be divided into two or more directions and FRCs are called orthotropic and isotropic with regard to the thermal and physical properties, respectively.

Variation of the fibre reinforcement type from continuous unidirectional (fibre bundle) to the continuous bidirectional (fibre weave) also makes a difference in the stress–strain diagram of the FRC material. Figure 9.4 shows the variation of high strength–high modulus for unidirectional FRCs to high-toughness FRCs with bidirectional fibres. The diagram shows a comparison of mechanical properties for various materials for the same construction. For example, the pontic of an FPD, or a root canal post, where high strength and rigidity are needed, can be reinforced with continuous unidirectional fibres. On the other hand, crown margins, where toughness is needed, can be reinforced with woven (bidirectional) fibres.⁶⁷ For comparison, Fig. 9.4 also shows that the conventional prosthetic materials of metal alloys and ceramics are brittle and cannot be tailor-made to have specific mechanical properties.

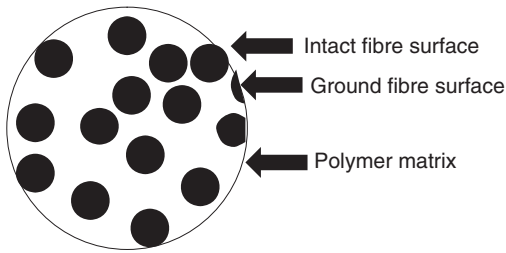


9.4 Stress-strain curve for FRCs with unidirectional and bidirectional fibres, and for conventional prosthetic materials (CoCr, cobalt chromium alloy; ZrO_2 , yttrium-stabilized zirconium dioxide; glass ceramic, Empress 2 type). Shaded area integrates the zero point and end points of the 0, 18, and 65 vol% curves.

There are several studies dealing with FRC strength that may have shown misleading values for the material strength. Testing of specimens of small dimensions, such as root canal posts, can lead to incorrect results. It is known that the mathematical formulae commonly used to calculate flexural strength and modulus of elasticity of test specimens are dependent upon the diameter (height) of the specimen and span length of the test set-up for the three-point bending test.⁶⁸ With a constant span length, thinner specimens reveal higher flexural strength and modulus of elasticity values than those obtained with specimens of the same material but of larger dimension. Thus, for comparison of material strength values, specimens should be of exactly the same diameter and span length in their test configuration. This is of importance in the interpretation of results obtained from root canal posts, for example.

9.2.2 Interfacial adhesion

Adhesion of particulate filler resin composite (PFC) (resin luting cement, veneering composite) plays an important role for load transfer from the surface of the device to the FRC framework and tooth. FRC as a bonding substrate contains different types of materials, from polymers to inorganic glass-fibre fillers and even particulate fillers (Fig. 9.5). Internal adhesion of the FRC influencing the cohesive strength of the FRC is based on bonding the fibres to the polymer matrix. In this respect, the most suitable fibres are OH-group-containing glass and silica fibres which can be silanated for improved adhesion to the polymer matrix.³⁷⁻⁴⁰ Less suitable fibres are UHMWP fibres which have proved to be difficult for resin adhesion even though the fibre surface has been activated with various types of high-energy treatment, for example.^{47,48}



9.5 Cross-sectional structure of FRC showing the multiphasic nature of FRC as an adhesional substrate for veneering composite or resin composite luting cement.

In bonding new resin to FRCs, the fibres and polymer matrix are substrates for adhesion. If the fibres of the FRC are exposed on the bonding surface, the adhesive properties of the fibres themselves play a role in bonding the adhesive resin and resin composite luting cement to the FRC: glass fibres can be bonded to partial fibre reinforcement (PFR) by silanation. Due to the cross-linked nature of the polymer matrix of most of the dental FRC materials, there are two possibilities for obtaining adhesion of the PFR to the FRC: mechanical interlocking or adhesion based on ongoing polymerisation of the resin matrix of the FRC. If the FRC contains non-cross-linked polymer phases, i.e. they are made of thermoplastics or semi-IPN polymers, the adhesion can also be based on diffusion of monomers of the new resin or resin composite into the non-cross-linked polymer matrix.^{57,58} This requires the solubility parameter of the linear polymer to be close to that of the monomer system of the PFR. In polymerisation of the resin, an adhesive bond based on a secondary semi-IPN structure is formed (Fig. 9.2). A well-known example of the secondary semi-IPN structure is found in repairs of fractured denture bases by repair acrylic resin. The repair acrylic resin monomers dissolve and swell the surface to form a durable secondary semi-IPN bond.^{69,70}

Adhesion of PFC to directly (or chair-side-) made FRC differs from FRC made indirectly in the dental laboratory. It is known that in polymerisation of resins and resin-based composites for FRCs in air, a non-polymerised surface layer, the so-called 'oxygen-inhibited layer', is formed on the surface.⁷¹ PFCs can adhere to this layer by free radical polymerisation of the PFR and form a durable bond.

9.3 Removable dentures

Research on dental FRCs started in the early 1960s when the first experiments on using glass fibres in denture base polymers were undertaken.

Besides the use of glass fibres, some tests were made of denture base polymers reinforced by carbon/graphite fibres. However, the reasons for the poor performance of fibres when they were used with powder-liquid-type denture base resins were not pursued at that time. In the 1990s, studies were published that showed that highly viscous resin mixtures of PMMA powder and monomer liquid were not able to impregnate around fibres adequately.^{52,53} The use of excess monomer liquid to lower the viscosity of the resin mixture did not resolve the problem. The higher quantity of monomer liquid in the resin mixture caused void formation in the composite by polymerisation contraction.⁵² This led to the development of the pre-impregnation system of reinforcing fibres with porous PMMA.⁷² Porous PMMA between the silanised glass fibres behaves similarly to a polymer powder in the acrylic resin mixture. It lowers the polymerisation shrinkage of the resin between the fibres.

Fibre reinforcement in denture bases can be divided into two categories. Ladizesky and co-workers reported a method whereby fibres were distributed throughout the entire denture base.^{6,7} On the other hand, the approach by Vallittu² is based on the concept that only the weakest part of the denture base – the location of fracture initiation – is reinforced by fibres. The two reinforcing concepts are called total fibre reinforcement (TFR) and partial fibre reinforcement (PFR).² Clinical studies have been performed with FRC-reinforced removable dentures^{2,73} suggesting that PFR offers an effective method of eliminating fractures in denture bases, as demonstrated by Narva.⁷⁴

The successful use of PFR requires the correct positioning of the fibres in the denture base.^{75,76} The fibres of the PFR should be placed in the region of the denture base where the fracture initiates. The correct place for the fibres in upper complete dentures is close to the denture teeth and fibres should be directed along the ridge lap in a horseshoe shape. Continuous unidirectional fibres offer the highest resistance against mid-line fractures. In removable partial dentures, where the fracture is likely to occur in the anterior margin of the denture, fibres in the form of a woven fabric are preferred. On average, a 10mm wide FRC region with woven glass fibres eliminates denture fracture initiation and propagation. Overdentures are also reinforced with woven fibres to eliminate denture base fractures of the polymer close to the precision attachments of the dentures. It has been suggested that FRCs can also reduce the problem of attachment loosening.

There has been discussion concerning the beneficial use of light-curing fibre reinforcement with a cross-linked polymer matrix using denture base polymers. It is known that the denture base polymer does not properly bond to the light-curing polymer matrix of the FRC. Therefore, light-curing FRC reinforcement is not the first choice of reinforcement for removable

dentures. The aim is to have a polymer matrix of reinforcing FRC that is chemically and structurally similar to that of the structure of the denture base polymer, i.e. non-cross-linked PMMA. This allows the denture base polymer to form a homogeneous polymer structure with the polymer of the denture base. Use of a polymer (PMMA)-pre-impregnated fibre reinforcement can produce an optimised reinforcing effect.^{75,76} Glass fibres in denture base polymers, even if they are exposed, do not show increased adhesion of *Candida albicans* to the material surface.⁷⁷

9.4 Fixed partial dentures

9.4.1 Permanent fixed partial dentures

FRCs can be used to produce definitive fixed partial dentures.⁷⁸ Based on the current clinical results, it is reasonable to expect FRC fixed partial dentures (FPDs) to have good longevity.⁷⁸ FPDs made of FRC are classified as surface-retained FPDs, inlay/onlay-retained FPDs, full coverage crown-retained FPDs and hybrid FPDs.⁷⁹ The latter type is a combination of various retaining elements according to the specific need of the dentition. FRC FPDs can be made directly or indirectly. Implant-supported FPDs have been fabricated from carbon/graphite FRC and glass FRC.^{80–82} All permanent-type, indirectly made, tooth-supported FRC FPDs have to be luted with resin composite luting cements, although there are reports that conventional luting cements have been evaluated.²⁰ Direct FRC FPDs can be bonded to tooth by polymerisation of restorative composite resins. The adhesive properties of FRCs bonded directly to the dentine and enamel have been studied by Tezvergil *et al.*^{83,84} showing that only minor differences could be found between the adhesive properties of FRC and PFC. In the FRC FPDs, the framework between the abutments is made of continuous unidirectional fibres which offer high flexural strength.^{67,85} The crowns can be reinforced with woven fibres or, in some fabrication concepts, by making a fibre loop of unidirectional fibres to surround the abutment.¹⁴ Recent clinical studies have shown that FRC frameworks need to provide support for the veneering resin composite and, therefore, additional fibres are required inside the pontic.¹⁵ There are also studies that emphasise the importance of the internal fibre geometry of the FRC framework to the strength of the FPD construction.^{86,87}

Surface-retained resin-bonded FPDs made of metals are normally supported and bonded from one end in order to reduce the number of debondings. In the case of surface-retained FRC FPDs, the bridgework can be supported from both ends because of better bonding characteristics and minor flexibility of the FRC framework.⁷⁹ The flexibility allows abutment teeth movement to occur to some extent without loosening the FPD. In the

surface-retained FRC FPDs, the location of the bonding wing in the vertical dimension of the abutment is important. Fibres of the bonding wing should be placed close to the incisal edge to eliminate the dislodging turning forces. On the other hand, the bonding wing needs to cover as large a surface as possible. The bonding wing is placed most often on the lingual surfaces of the abutments but labial and buccal surfaces can also be used. To protect the fibres of the bonding wings, a layer of PFR is placed to cover the wings. In this situation, good interfacial adhesion between the FRC framework and the particulate filler resin composite is important to avoid chipping of the resin composite. In connectors, the continuous unidirectional fibres should have a cross-sectional design which offers good resistance against occlusal forces. It has been shown that the thickness of the connector versus the width of the connector is an important parameter when stiffness and strength are optimised. Normally the cross-section of the connector will be full of fibres, but if there is excess of space, the highest strength is provided by placing the fibres towards the tension side.⁸⁵ Surface-retained FRC FPDs are used in the anterior and premolar regions. Recent laboratory investigations have suggested that optimally designed FRC FPDs made on non-prepared abutments can provide an even higher load-bearing capacity than conventional porcelain-fused-to-metal FPDs.⁸⁸

Inlay/onlay-retained FPDs are made by placing continuous, unidirectional fibres in the abutment cavities. The FPD can be made indirectly or directly. In a canine, it is recommended that an additional bonding wing be placed buccally or palatally to the framework to avoid loosening of the inlay in a canine-protected occlusion. In the case of existing old fillings, removal of the filling normally provides space for the FRC framework and veneering resin composite. Vertical support against occlusal loads is needed and, in intact teeth, a proximal box preparation with a depth of more than 1 mm will provide support for the FPD if the fibres are accurately placed into the box.⁸⁸ The load-bearing capacity of such FPDs is higher than the maximal biting forces in the molar region.⁸⁹ Veneering of the FRC framework is completed using laboratory veneering resin composite or by restorative resin composite. Optimal thickness of the veneering resin composite on the occlusal surface of FRC frameworks is more than 1.5 mm.^{90,91}

Full coverage crown-retained FPDs are made by layering woven FRC on to prepared abutments. Abutments are connected with continuous unidirectional fibres with additional pieces of FRC to support cusps or the pontics. Veneering is made with laboratory particulate filler resin composite. The FRC framework is intended to be fully covered by veneering composite in order to obtain a polishable and tooth-coloured surface. Special attention needs to be paid to the interproximal regions. If the FRC framework is not properly covered by the veneering composite, or preferably opaque paint, the darkness of the oral cavity can be transmitted through the connectors

and cause cosmetic/aesthetic problems. CAD-CAM-processed FRC blocks made of short random-fibre-oriented FRC in a polyamide matrix (nylon) are also available for FRC framework fabrication. The mechanical properties of short FRCs are considerably lower than those of continuous unidirectional FRCs.⁶⁵ The water sorption of polyamide causes reduction of the flexural strength of the FRC by up to 60% in 30 days.⁹²

9.4.2 Provisional fixed partial dentures

Provisional FPDs can be reinforced with fibres, as has been shown in several investigations.^{67,85,93–96} The positioning of the fibre-rich layer plays a significant role in the load-bearing capacity. Optimally, continuous unidirectional fibres should be placed close to the region of highest tensile stress in the FPD. In order to avoid fractures of crown margins, the crowns can be reinforced with woven fibre fabrics.⁶⁷ If the provisional FPD is made of the powder–liquid type of acrylic resin, the polymer-pre-impregnated glass-fibre reinforcement provides the highest reinforcing efficiency. Provisional FPDs made of auto-mix temporary resins, can also be reinforced with light-curing resin-impregnated FRCs. Some attempts have been made to incorporate antimicrobial substances in to FRCs used in temporary FPDs.⁹⁷

9.5 Periodontal splints and retainers

Periodontal splints and orthodontic retainers made of FRCs are most often based on using continuous unidirectional FRCs of smaller diameters than in FPDs. Positioning of the fibres on etched enamel follows the same principles used in surface-retained adhesive FPDs. The fibres should be placed in the region of highest tensile stress. In the anterior region these exist close to the incisal edge from where the de-bonding begins. In molar regions, the fibres are normally placed into continuous occlusal cavities and covered with a layer of PFC. In order to protect the FRC from mechanical damage and from oxygen inhibition during polymerisation, a layer of PFC (hybrid or flowable resin composite) is applied on the FRC surface. The preliminary clinical outcomes of FRC periodontal splints have been encouraging.³²

9.6 Root canal posts

The use of FRCs in root canal posts to anchor cores and crowns has rapidly increased.^{27,29,30,62,98} FRCs can be used in root canals as (a) prefabricated posts and (b) individually formed posts (Table 9.3). The prefabricated posts are made of reinforcing fibres (carbon/graphite, glass, quartz) and a fully polymerised resin matrix between the fibres forming a solid post with a predetermined diameter. Individually formed posts are made

Table 9.3 Summary of the mechanisms for bonding composite resin luting cements to the FRC post

Type of post	Type of fibre	Type of polymer matrix	Bonding mechanism
Prefabricated	Carbon/graphite	Cross-linked	Mechanical retention
Prefabricated	Glass or quartz	Cross-linked	Mechanical retention Silane-promoted adhesion
Individually formed (laboratory made)	UHMWP	Cross-linked	Mechanical retention
Individually formed (laboratory made)	Glass or quartz	Cross-linked	Mechanical retention Silane-promoted adhesion
Individually formed (laboratory made)	Glass	Semi-IPN	Mechanical retention Silane-promoted adhesion Secondary semi-IPN adhesion
Individually formed (chair-side made)	UHMWP, glass or quartz	Cross-linked	Mechanical retention
		Semi-IPN	Silane-promoted adhesion Secondary semi-IPN adhesion Free radical polymerisation of adhesion

of non-polymerised fibre–resin–pre-impregnated posts, consisting typically of glass fibres and light-curing resin matrix. The rationale of the individually formed FRC post is to fill the entire space of the root canal with FRC material.^{99–101} The increased fibre quantity, especially in the coronal part of the root canal increases the load-bearing capacity of the system and the biomechanics of a tooth can be better simulated because of the fibres located closer to the dentine, where highest stresses exist. Due to some contradictory *in vitro* results on the potential benefits of the individually formed post with metal crowns¹⁰² further research into this topic is required.

A tooth restored with a root-canal-post system should be able to withstand cyclic loading of high magnitude for a long period of time without catastrophic failure or marginal breakdown of the crown, which can predispose the patient to secondary caries. The load-bearing phase of the root-canal-post system, i.e. the FRC root canal post, should withstand the loads

and the crown margins should remain intact. Repeated stress cycles cause microscopic cracks: mainly in the tension side of the construction and, after a period of time, a number of cracks will increase to such a size that a sudden fracture can occur even with a low stress level. Clinically, the material-based weak fatigue resistance is compensated by designing and dimensioning the cast metal or FRC post-and-core correctly, thus increasing the quantity of reinforcing fibres in the cervical region of the tooth. This approach can be taken into consideration by fabricating an individually formed post instead of using a prefabricated post.

Fabrication of prefabricated FRC root canal posts is based on impregnation of fibres with thermoset resins, such as dimethacrylate or epoxy resins. Thermoset resins forming the cross-linked polymer between the fibres do not allow good bonding of the post to the resin cement (Fig. 9.2). In order to overcome the problem of adhesion, some manufacturers have added serrations to the post for mechanical retention to the cement. On the other hand, if the semi-IPN polymer matrix is used between the fibres, as can be the case in individually formed posts, adhesion of the post to the cement is good.^{27,98} It has been shown by radioactive-labelled resins that monomers of an adhesive resin diffused into the semi-IPN polymer matrix of the post to a depth of 25 µm in a few minutes. These resins should also enable complete impregnation of the fibres. Unfortunately, there are some prefabricated FRC root canal posts on the market that do not entirely fulfil the requirement of complete impregnation and, thus, the strength of the post is lower than expected from the constituents.⁵⁹

9.7 Future trends

A variety of dental FRC materials are available and they improve the mechanical strength of the resins and particulate filler composites. The light-curing resin-impregnated continuous unidirectional FRC materials can provide similar bend strength values to those measured from cast cobalt chromium alloy or yttrium-stabilised zirconium dioxide. However, the properties are anisotropic: the reinforcing effect is available only in one direction for the fibre-reinforced material. This, therefore, requires that the dental professional better understands the biomechanics of the dentition and design principles of FRC devices. If the reinforcing effect of the fibres is divided in several directions, the maximum strength values are considerably lower. On the other hand, the toughness of the material is increased.

There has been critical discussion among prosthodontists about whether FRC devices are permanent, semi-permanent, long-term temporary or temporary in nature. The current opinion based on materials science and clinical experience suggests that FRC devices, if they are made of high-quality materials and designed correctly, fulfil device requirements for long-term

use. Therefore, the FRC FPDs are defined as definitive solutions. Furthermore, taking into consideration that the fabrication of many of the fixed FRC devices require only minimal if any tooth preparation, it can be stated that FRCs provide a modern adhesive alternative for single and multiple tooth replacements. The use of FRC FPDs is not limited to single tooth replacements. FRC FPDs can be used in the fabrication of multiple-unit restorations of inlay, complete coverage crown or hybrid FPD design. Of these, the hybrid FPDs provide greatest benefit to the patient by lowering the biological price of the treatment, i.e. preserving tooth substance, making it at the same time more economical. The long-term cost–benefit ratio of FRC FPDs versus conventional FPDs or implant-retained FPDs needs to be evaluated.

Furthermore, based on studies of the biomechanics of teeth and through clinical experience, from the early 1990s, it is suggested that the use of FRC root canal posts provides a good alternative to cast metal posts which are more technique-sensitive in fabrication. However, criticism needs to be focused on the load-bearing capacity of FRC root canal posts of small diameter. Thus, thin FRC posts do not necessarily provide enough strength for the crown–core–post–root–bone complex and this may lead to breakdown of the adhesive interface of core build-up composite to dentine and marginal secondary caries. In principle, the alternative FRC post design of individually formed posts provides a solution to this problem.

Future development in FRCs is focused on the optimisation of the design of substructures in FRC devices. Attempts to use the semi-IPN polymer matrix short-glass FRC in restorative filling material applications have also been made. This is one field of future development for dental FRCs.

9.8 Summary

FRCs have been introduced for use in a variety of clinical applications. FRC is composed of reinforcing fibres which are embedded in resin matrix. At present, the continuous unidirectional glass FRC provides the highest strength for the dental FRC. Several parameters, including the fibre volume fraction and fibre direction, considerably affect the properties of FRCs which can be anisotropic, orthotropic or isotropic. Clinically, the FRC material is used in removable dentures, fixed partial dentures, periodontal splints, orthodontic retainers and root canal posts. At present, FRCs can produce definitive, as opposed to provisional, prostheses. The longest and most encouraging clinical experience is obtained with removable dentures and prefabricated root canal posts. In addition, other applications benefit from the use of FRC material as an alternative for metal alloys and all ceramics.

The correct use and understanding of design principles for FRC devices provides minimally invasive long-term restorations even for multiple tooth replacement.

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Fracture mechanics characterization of dental biomaterials

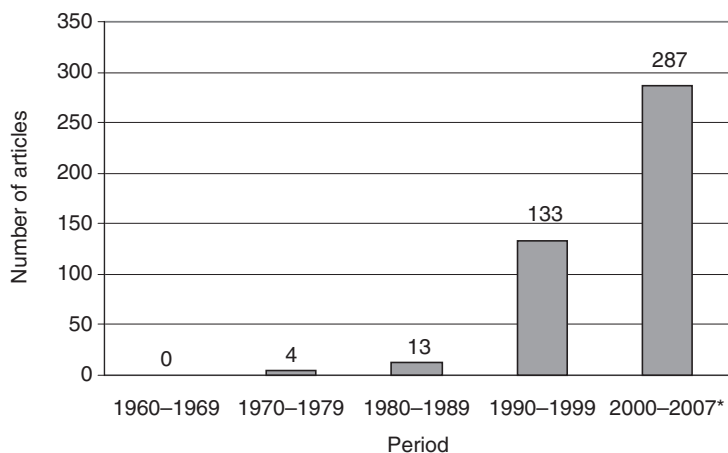
N. D. RUSE, The University of British Columbia, Canada

10.1 Introduction

Every year, there are several hundreds of articles published in the peer-reviewed literature and many more hundreds of posters or oral presentations reporting results of mechanical tests on dental materials. It is therefore rather astonishing to realize the minimal correlation that exists between the available *in vitro* data on mechanical properties and the *in vivo* performance of dental materials. Moreover, the *in vitro* data on mechanical properties are poor predictors for the long-term *in vivo* performance of dental materials. The Technical Committee 106 (Dentistry) of the International Organization for Standardization (ISO), which is responsible for standards for dental materials, often finds it difficult to establish minimum values for given properties and has been forced over the years to reduce previously set values since it could not find strong evidence justifying the settings (e.g. ISO 9917-1, compressive strength). One of the papers originating from a symposium organized by the American Association for Dental Research (AADR) during its 2006 annual meeting in Orlando, Florida, concluded that:

The results of bond strength tests did not correlate with laboratory tests that evaluated the marginal seal of restorations such as microleakage or gap analysis. The quantitative marginal analysis of Class V fillings in the laboratory was unable to predict the performance of the same materials *in vivo*. Therefore, microleakage tests or the quantitative marginal analysis should be abandoned and research should focus on laboratory tests that are validated with regards to their ability to satisfactorily predict the clinical performance of restorative materials.¹

The identified lack of correlation and of predictability may explain the shift in focus of the dental materials research community over the past 10–15 years towards the application of fracture mechanics methodology for the characterization of both dental materials and their adhesive interfaces. The shift can be substantiated through a simple literature search of published



*Up to May 2007

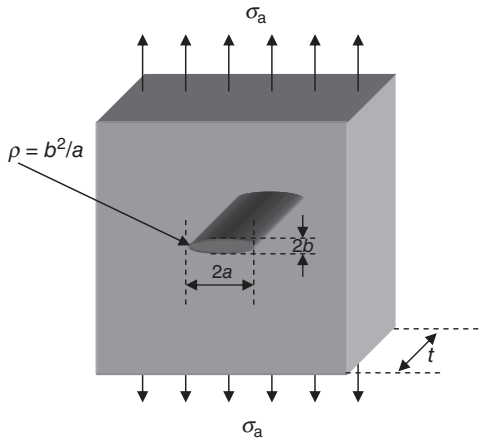
10.1 Dental-related fracture mechanics articles (1960-2007; Web of Science).

articles, using Web of Science and the search criterion '*dent* and (fracture toughness or fracture mechanics)*', the results of which are summarized in Fig. 10.1.

The aim of this chapter is to review briefly some fundamental aspects of fracture mechanics and the application of fracture mechanics methodology to the characterization of dental hard tooth tissues, dental materials, and their adhesive interfaces.

10.2 Theoretical considerations

Fracture mechanics is a relatively young discipline, the foundations of which are regarded as having been laid by the pioneering work of Griffith,² Irwin,³ and Orowan⁴ early in the twentieth century. In general, the characterization of brittle materials/interfaces should be based on fracture mechanics investigations.⁵ Flaws in brittle materials, unlike ductile materials, do not allow the blunting of a crack and the relaxation of concentrated stresses. Consequently, the fracture is initiated at the critical flaw and usually propagates catastrophically through the specimen.² Therefore, the strength of a brittle material/interface is governed by the probability that a defect of critical size will be encountered, a probability that can be described by a Weibull function.^{6,7} The close link between the presence of defects in brittle materials/interfaces and their unpredictable catastrophic fracture makes performance sensitive to processing conditions. The theoretical considerations of Inglis⁸ have shown that the stress $\sigma_{\max}$ at the tips of internal elliptical cracks/defects



10.2 Body with internal elliptical flaw subjected to tensile stresses.

present in an infinite body (see Fig. 10.2) is significantly higher than the stress applied (σ_a) and is directly proportional to the crack length (a) and inversely proportional to the crack radius (ρ).

$$\sigma_{\max} = \sigma_a (1 + 2\sqrt{a/\rho}) \approx 2\sigma_a \sqrt{a/\rho} \quad [10.1]$$

The radius (ρ) at the tip of an elliptical defect is given by:

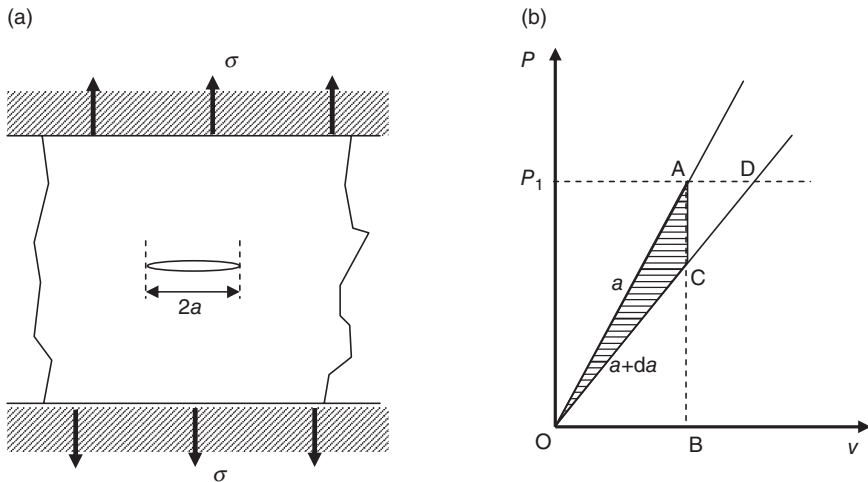
$$\rho = b^2 / a \quad [10.2]$$

It should be noted that for internal cracks, the crack length is denoted by $2a$ while for external cracks, the crack length is denoted by a . The stress concentration at crack tips can lead to crack propagation and eventually to the catastrophic failure of materials under applied stresses significantly lower than the strength of materials. Based on theoretical considerations related to attractive and repulsive forces between atoms, it can be estimated that the cohesive strength (σ_c) of a material is approximately equal to one third of the modulus of elasticity (E) of the material, or further estimated by:⁹

$$\sigma_c = \sqrt{\frac{E\gamma}{a_0}} \quad [10.3]$$

In equation [10.3], a_0 is the equilibrium distance between atoms and γ is the characteristic free surface energy of the material.

Griffith,² based on the work of Inglis,⁸ approached the analysis of crack propagation in a material with an internal defect subjected to external loading from an energy balance point of view. He postulated that a crack would extend if the internal energy of a body resulting from the application of external forces (dU/da) equals the energy required to create the new



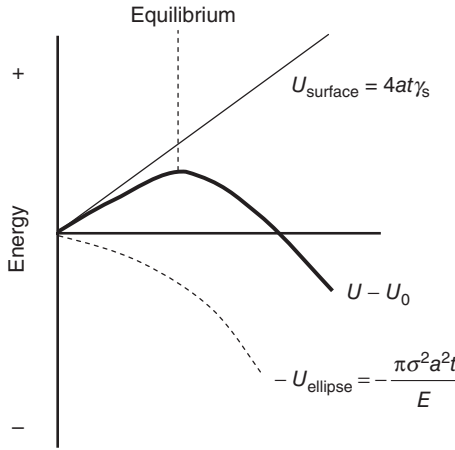
10.3 *a* Fixed grip condition for a body with an internal elliptical flaw subjected to tensile stresses; *b* load versus displacement curve.

surfaces associated with the extension of the crack (dW/da ; equation [10.4]). Since the energy required to create the new surfaces opposes crack growth, it is referred to as crack resistance, R .

$$\frac{dU}{da} = \frac{dW}{da} \quad [10.4]$$

In a fixed grip situation, a sample with an elliptical crack is stressed to a stress σ and fixed at its ends (Fig. 10.3a). The area OAB in Fig. 10.3b is the energy stored in the plate under these conditions. Should this energy be sufficient for crack growth, the crack would extend by da , which under the fixed grip conditions would lead to a relaxation of the load from A to C and a consequent drop in energy given by the area of the triangle OAC . This drop in energy is associated with the da crack extension. Under fixed grip conditions, the crack will extend until the available energy is equal to the energy required for the formation of new surfaces.

Griffith² evaluated the energy balance under the fixed grip condition through equation [10.5]. The energy difference between the internal energy of a body before (U_0) and after (U) the introduction of an elliptical crack in the presence of an external stress (σ) is given by the decrease in energy associated with the presence of the crack and the increase in energy associated with the creation of two new surfaces, each of an area equal to $2at$ and having an associated surface energy γ_s (see Fig. 10.2).



10.4 Energy balance.

$$U - U_0 = \frac{\pi\sigma^2 a^2 t}{E} + 4at\gamma_s \quad [10.5]$$

A graphical representation of the energies considered is presented in Fig. 10.4. Equilibrium between the driving force (decrease in energy associated with the presence of the crack) and the retarding force (increase in energy associated with the creation of two new surfaces) is reached when the slope of the resultant curve equals zero, i.e. when the derivative of equation [10.5] with respect to crack length, a , equals zero:

$$\frac{\partial U}{\partial a} = 4t\gamma_s - \frac{2\pi\sigma^2 at}{E} = 0 \quad [10.6]$$

Reduction of terms in equation [10.6] leads to the equilibrium condition:

$$2\gamma_s = \frac{\pi\sigma^2 a}{E} \quad [10.7]$$

In equation [10.7], $2\gamma_s$ is the crack resistance, R , and $(\pi\sigma^2 a)/E$ is G , the energy release rate. Re-writing equation [10.7], Griffith has established the relationship between stress, modulus of elasticity, and energy release rate for plane stress* (equation [10.8]) and plane strain* (equation [10.9]) conditions (where ν is the Poisson's ratio):

$$\sigma = \sqrt{\frac{2E\gamma_s}{\pi a}} = \sqrt{\frac{EG}{\pi a}} \quad [10.8]$$

* In thin plates loaded perpendicular to their small dimension, the three components of stress are zero for the two faces that are closest to each other, thus creating a state of plane stress. In thick plates, the bulk and unstressed material constrains the extent of deformation in one direction near the crack tip, thus creating a state of plane strain.

$$\sigma = \sqrt{\frac{2E\gamma_s}{\pi a(1-\nu^2)}} = \sqrt{\frac{EG}{\pi a(1-\nu^2)}} \quad [10.9]$$

The energy release rate, or the crack driving force, represents the energy available for crack growth in a body under a given stress (σ) and in the presence of a crack of length a . The second derivative of equation [10.5] characterizes the nature of the equilibrium reached and, since it is negative (equation [10.10]), it indicates that the equilibrium is unstable and that once reached the crack will grow.

$$\frac{\partial^2 U}{\partial^2 a} = \frac{2\pi\sigma^2 t}{E} \quad [10.10]$$

At the point of instability, the increase in load has lead to a critical stress, σ_c , and the critical energy release rate has reached a critical value, G_c , equal to the energy required for the formation of new surfaces, R . In mode I loading, i.e. in tension, this value is symbolized by G_{IC} , which can be determined by measuring the stress required to fracture a plate containing a crack of size $2a$ and using equations [10.8] or [10.9].

The determination of G_{IC} can also be achieved by investigating the change in compliance of a specimen caused by the change in size of an existing crack within it. Thus, in a constant load situation, the energy balance (equation [10.11]) involves the elastic energy stored in the body (U), the work done by the external forces (F), and the resistance to crack propagation W .

$$U - F + W = 0 \quad [10.11]$$

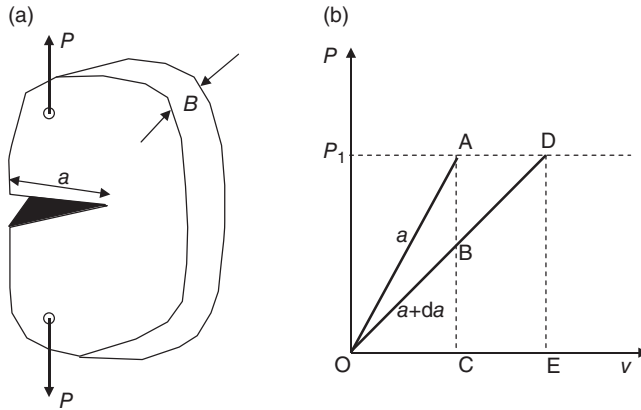
Under the application of external forces, the load-application points of a cracked plate of thickness B (Fig. 10.5a) will undergo a displacement v that will be reduced by a quantity dv when the crack extends by da . The corresponding energy change can be expressed as:

$$\frac{dF}{da} = \frac{P}{B} \frac{dv}{da} \quad [10.12]$$

As long as there is no crack growth, v is proportional to the applied load and can be calculated from the compliance (C) of the plate:

$$v = CP \quad [10.13]$$

The compliance of an uncracked plate of modulus E , length L , thickness B , and width W is given by equation [10.14] and the elastic energy (U) stored in such a plate is given by equation [10.15].



10.5 a Plate with surface crack subjected to constant tensile loads;
b load versus displacement curve used for compliance and graphical
determination of the critical energy release, G_{IC} .

$$C = L/WBE \quad [10.14]$$

$$U = \frac{1}{2} P v = \frac{1}{2} C P^2 \quad [10.15]$$

Equation [10.16] describes the equilibrium state where, as in the case of fixed grips, the derivative of the resulting energy as a function of crack growth (da) equals zero.

$$G_{IC} = \frac{d}{da}(F - U) = \frac{dW}{da} \quad [10.16]$$

Considering equations [10.13] and [10.15], equation [10.16] can be re-written as equation [10.17], which, after cancellation of terms, yields equation [10.18].

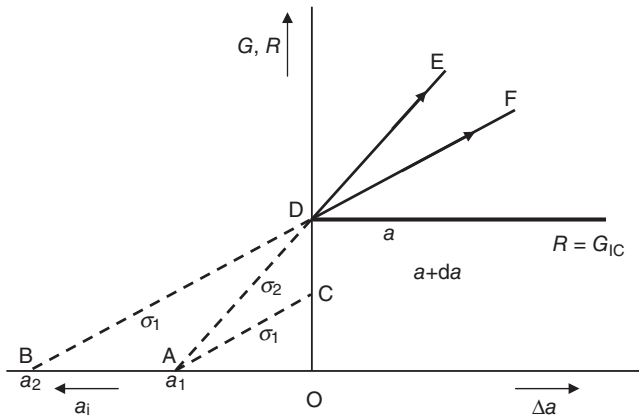
$$G_{IC} = \frac{1}{B} \left(P \frac{dv}{da} - \frac{dU}{da} \right) = \frac{1}{B} \left(P^2 \frac{\partial C}{\partial a} + CP \frac{dP}{da} - \frac{1}{2} P^2 \frac{\partial C}{\partial a} - CP \frac{dP}{da} \right) \quad [10.17]$$

$$G_{IC} = \frac{P^2}{2B} \frac{\partial C}{\partial a} \quad [10.18]$$

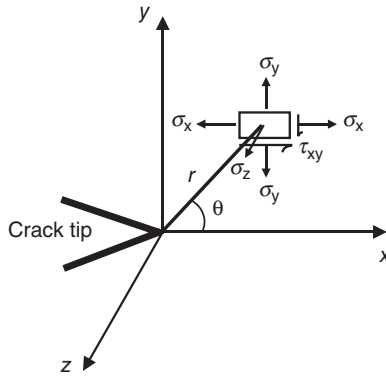
It is apparent from equation [10.18] that G_{IC} can be obtained for any specimen for which the compliance calibration ($\partial C/\partial a$) had been determined by noting the load at fracture, P .

A graphical derivation of G_{IC} is also possible. Line OA in the load–displacement diagram in Fig. 10.5b shows the elastic response of a body with a crack of size a , subjected to constant loads. For a larger crack size, i.e. $a + da$, the compliance of the sample changes and line OD is obtained. Considering that the crack lengthening from a to $a + da$ occurs at load P_1 , one could analyse both the fixed grip situation and the increasing load situation. In a fixed grip situation, the displacement remains constant while the load drops from A to B as a result of crack extension and the energy consumed in that process is equal to the area OAB. In a constant load situation, the crack extension would lead to a change in compliance from OA to OD and the energy consumed would be equal to the area OAD. The difference between the two scenarios is the small, negligible energy corresponding to the area ABD and, therefore, it could be concluded that the energy available for crack growth is the same in both cases. Under fixed grips, it is delivered by the elastic energy while in the constant load it is delivered by the applied load.

A generalized description of the criterion for crack growth could be presented by discussing the diagram in Fig. 10.6. The diagram describes the behaviour of a body with different crack sizes, subjected to constant loads. Thus, when the internal crack size is a_1 and the stress level is σ_1 , the value of G is inferior (point C) to $R = G_{IC}$ that is depicted as a straight line. Increasing the load increases both the stress as well as the value of G ; at a stress σ_2 , G equals G_{IC} (point D) and crack extension can take place. Beyond point D, under constant load, G will always be larger than G_{IC} (line AE) and therefore the crack will continue to extend. For an original crack a_2 larger than a_1 , the lower stress level σ_1 is sufficient to raise G to the level of G_{IC} (point D on line BF), leading therefore to crack extension.



10.6 Generalized energy analysis.



10.7 Crack tip stresses in polar coordinates.

Griffith's energy approach established a required condition for crack growth and, for perfectly elastic and perfectly brittle materials, a sufficient one as well. However, any departure from these conditions renders the energy approach invalid.

It was Irwin³ who first attempted to approach the crack propagation issue from a stress perspective. He was able to describe the stress distribution at any point around the crack tip (see Fig. 10.7) by using a set of polar axes (where the distance r from, and the polar angle θ relative to, the crack tip characterize the position of each point) and the set of equations [10.19].

$$\begin{aligned}\sigma_x &= \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left(1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right) \\ \sigma_y &= \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left(1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right) \\ \tau_{xy} &= \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \sin \frac{\theta}{2} \cos \frac{3\theta}{2}\end{aligned}\quad [10.19]$$

From the set of equations [10.19], it is apparent that by knowing K_I (I stands for opening or mode I loading) the complete set of stresses at any point around the crack tip could be determined. The term K_I is the stress intensity factor, expressed in $\text{MPa m}^{1/2}$ in order to ensure that the calculated stress is expressed in MPa. The stress intensity factor is a measure of the stress singularity at the crack tip. Its magnitude is determined by the stress applied, σ , the length of the surface crack or one-half the length of the internal crack, a , and a dimensionless functionality term Y dependent on the configuration of the cracked test specimen and the manner in which the loads are applied [10.20].⁹

$$K_I = Y\sigma\sqrt{\pi a}\quad [10.20]$$

When the applied stress is increased, K_I reaches a critical value, K_{IC} , leading to crack propagation. The critical value of the stress intensity factor, K_{IC} , describes the ability of a material/interface to withstand unstable crack propagation and is known as fracture toughness. The stress analysis proposed by Irwin established a required and sufficient condition for crack growth. Fracture toughness is an intrinsic material property and, considering equation [10.20], the higher the K_{IC} of a brittle material/interface, the higher the stress (σ) it can withstand for a given size of internal flaw (**a**).

For the ideal conditions of fixed-mode crack propagation and material complying with the assumptions of the theory of elasticity, fracture toughness can be expressed through the critical value of either the stress intensity factor, K_{IC} (expressed in $\text{MPa m}^{1/2}$), or the energy release rate, G_{IC} (expressed in J m^{-2}), introduced earlier. Under these conditions, the two expressions for fracture toughness (K_{IC} and G_{IC}) are equivalent, and can be calculated from one another knowing the modulus of elasticity E .^{9,10} Equations [10.21] and [10.22] express this equivalence for plane stress and plane strain conditions, respectively.

$$K_{IC} = \sqrt{EG_{IC}} \quad [10.21]$$

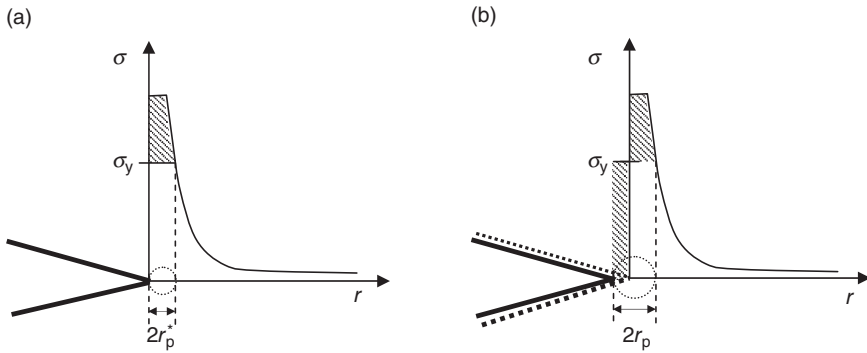
$$K_{IC} = \sqrt{\frac{EG_{IC}}{1-\nu^2}} \quad [10.22]$$

The energy analysis (G_{IC}) is rendered invalid for materials that do not comply with the assumptions of the theory of elasticity since plastic deformation occurs in the vicinity of the crack tip leading to energy dissipation. Irwin¹¹ and Orowan⁴ attempted to correct Griffith's energy balance analysis by introducing a plastic deformation energy term (γ_p) into equation [10.8], yielding:

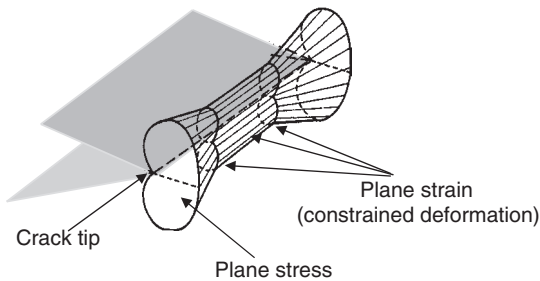
$$\sigma = \sqrt{\frac{2E(\gamma_s + \gamma_p)}{\pi a}} \quad [10.23]$$

However, difficulties related to an accurate estimation of the magnitude of γ_p ¹² render the energy approach unsuitable for materials that exhibit large plastic deformations.

The stress analysis (K_{IC}) remains valid as long as the plastic deformation area around the crack tip remains small compared with the K -dominant area. An analysis of the stresses near the crack tip (see Fig. 10.8a) shows that they tend towards infinity. Since the yield stress of the material (σ_y) is reached, the material at the crack tip will plastically deform and create a zone of plastic deformation of a radius r_p^* . Such a structure would behave as if the crack size has been extended by r_p^* and a new virtual crack tip and its stress environment have to be re-evaluated (Fig. 10.8b). A new plastic zone



10.8 a Stresses and plastic zone size at crack tip; b subsequent iteration of stresses and plastic zone size at crack tip.



10.9 Constrained plastic deformation in thick plates (plane strain).

is then considered and through serial iterations the extent of the plastic zone, r_p , at the crack tip can be estimated.¹⁰ Several approaches, by Irwin, Dugdale, Duffy, and others,¹⁰ have been made to estimate the size of the plastic zone yielding similar results and demonstrating that it is directly proportional to the square of the ratio of fracture toughness to yield strength:

$$r_p \propto (K_{IC}/\sigma_y)^2 \quad [10.24]$$

This implies that in order to estimate the size of the plastic zone, an estimated value of the fracture toughness is required.

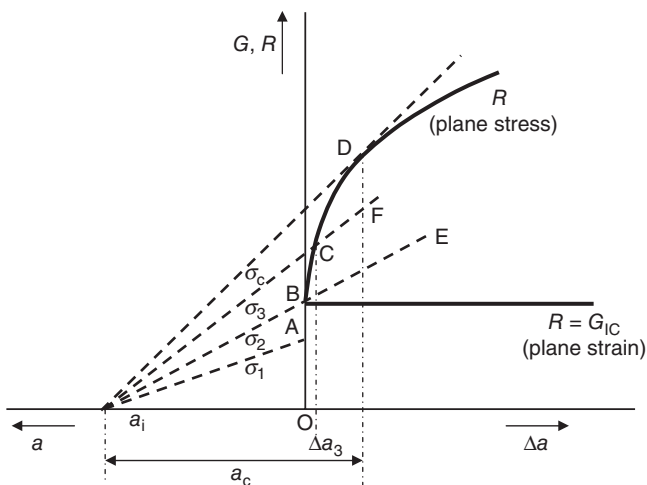
As previously stated, for valid K_{IC} determinations, the size of the plastic zone, r_p , has to be small compared with the K -dominant area.¹³ Under plane strain conditions, the bulk of the unstressed material confines the plastically deformed zone (see Fig. 10.9) and, for all practical purposes, there is no correction required in the calculation of K_{IC} . In order to ensure plane strain conditions, it has been experimentally determined that the ratio of the plastic zone, r_p , to the specimen thickness, B , has to be in the order of 0.025.¹⁰ Considering the estimates of the plastic zone, this condition translates into

the requirement that the crack size a and the thickness B of specimens, in order to ensure valid plane strain conditions, have to be equal or larger than 2.5 times the square of the fracture toughness to yield stress ratio:⁹

$$a, B \geq 2.5 \left(\frac{K_{IC}}{\sigma_y} \right)^2 \quad [10.25]$$

The theoretical considerations have focused so far on materials that comply with the assumptions of the theory of elasticity and with conditions of plane strain that minimize the effects of departure from elasticity. It should be underlined that valid fracture toughness (K_{IC}) values are those obtained under these conditions only. The interest in the fracture mechanics characterization of materials has led to the expansion of the methodology to elastic plastic materials and to plane stress conditions. Under these circumstances, it is possible for the resistance to crack propagation to change with increasing crack length resulting therefore in a changing R , as illustrated in Fig. 10.10. The conditions of crack extension for a material with a variable R curve (plane stress) are similar to those discussed for an elastic material, i.e. the crack will extend when the G_I equals or exceeds R . For a sample with a crack size a_i , this condition is achieved at stress σ_2 (point B). It can be seen that, for this sample, a stable crack growth will occur between stress σ_2 and σ_3 (points B and C) and up to the critical stress σ_c (point D). Once σ_c is reached and the crack has grown to a critical size a_c , the value of G_I will always be larger than R leading to unstable crack growth.

When G_I or K_I analyses cannot be performed due to significant plastic deformations, a so-called ' J integral approach' can be undertaken. Briefly,

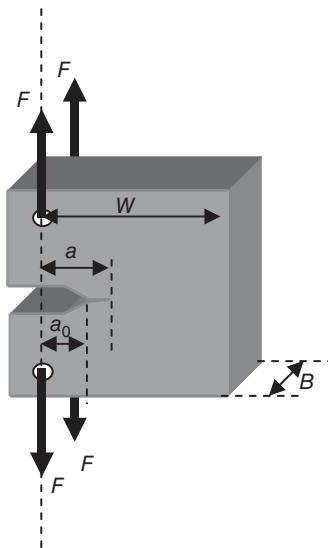


10.10 Generalized R -curve energy analysis.

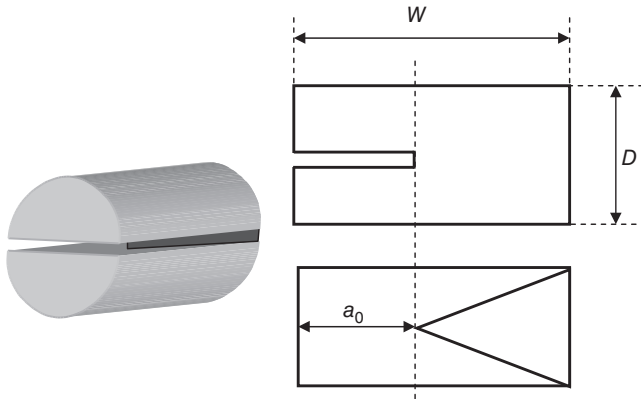
the J integral approach estimates the energy associated with crack growth by considering contour integrals around the crack tip that are path independent.¹⁰ Since the J integral approach could be applied for both elastic and elastic-plastic materials, it has been proposed as a more universal fracture criterion than G . Analogous to the determination of G_{IC} , J_{IC} could be determined through compliance analysis. A more in-depth discussion of the limitations of the J integral approach can be found in the books by Broek,¹⁰ Dowling,¹³ and Hertzberg.⁹

10.3 Determination of fracture toughness

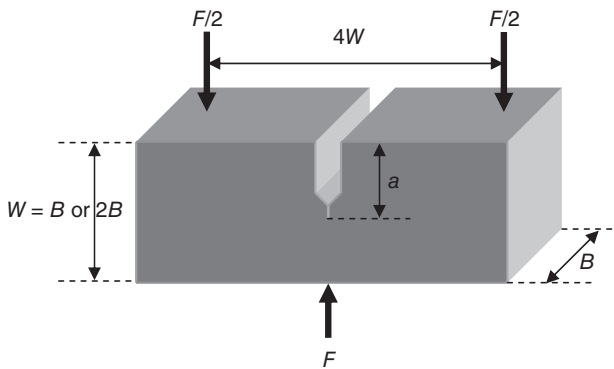
Since fracture toughness is an intrinsic material property that describes the ability of a material/interface to withstand unstable crack propagation, its determination represents an important aspect in the characterization of materials/interfaces. The determination of fracture toughness constitutes the focus of several international standards.^{14–19} The main scope of standardization is to ensure that the results obtained represent true and reproducible plane strain fracture toughness values. The standards provide detailed descriptions of specimen configuration and rigorous requirements as to the specimen size necessary to ensure plane strain conditions at the crack tip, along with details regarding test parameters and data interpretation. Several specimen configurations have been commonly used for the characterization of dental hard tooth tissues and dental biomaterials. They comprise the



10.11 Compact tension (CT) specimen.

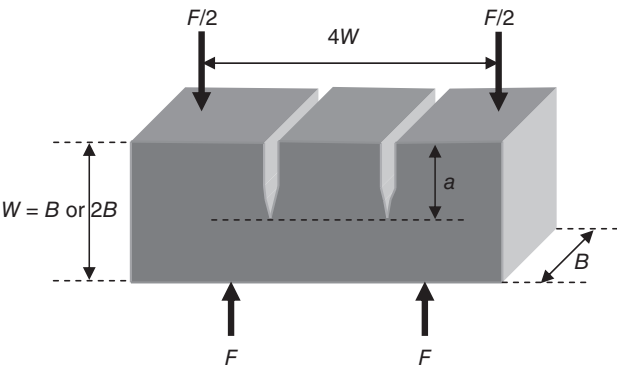


10.12 Chevron-notched short rod (CNSR) specimen.

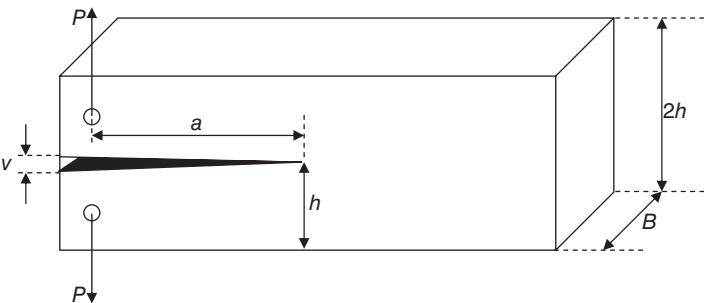


10.13 Single-edge-notched beam (SENB) specimen.

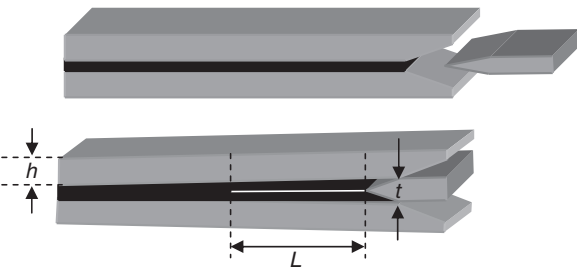
compact tension (CT) specimen^{17,19–22} (Fig. 10.11), the chevron-notched short rod (CNSR) specimen^{16,20,23–27} (Fig. 10.12), the chevron-notched beam (CNB) specimen,^{28,29} the single-edge-notched beam (SENB) three-^{20,28,30–32} or four-^{33–35} point bend specimen (Fig. 10.13), the double-notched bar four-point bend specimen³⁶ (Fig. 10.14), the double-cantilever beam (DCB) specimen³⁷ (Fig. 10.15), the DCB wedge specimen^{38,39} (Fig. 10.16), the DCB torsion specimen^{20,40} (Fig. 10.17), the tapered DCB specimen⁴¹ (Fig. 10.18), and the notchless triangular prism (NTP) specimen^{42–45} (Fig. 10.19). Macro-, micro-, and nano-indentation tests⁴⁶ (Fig. 10.20) have been widely used to determine the fracture toughness of dental ceramics.^{28,29} The cited references describe the tests and provide the formulae used to calculate fracture toughness.



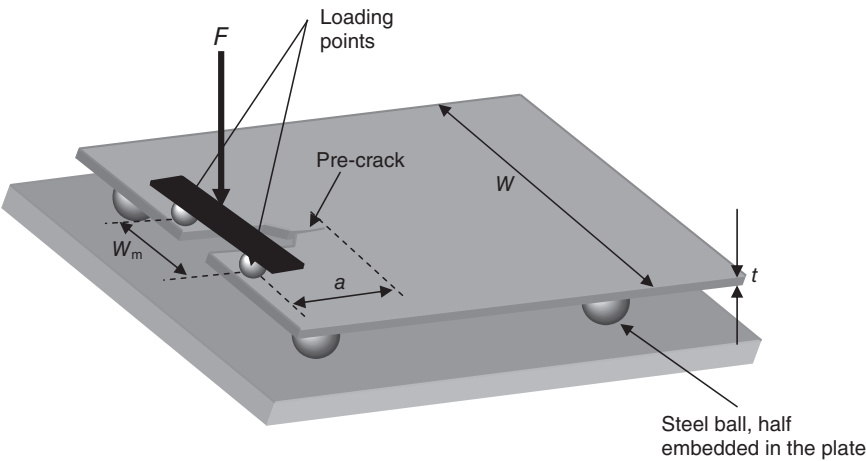
10.14 Single-edge double-notched beam (SEDNB) specimen.



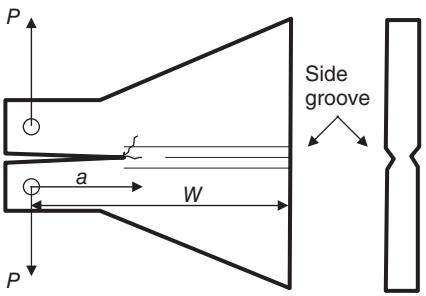
10.15 Double-cantilever beam (DCB) specimen.



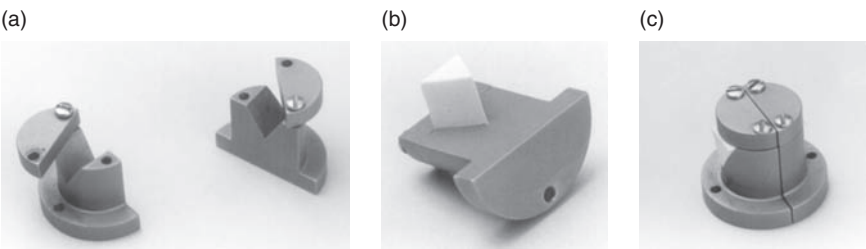
10.16 Double-cantilever beam (DCB) wedge specimen.



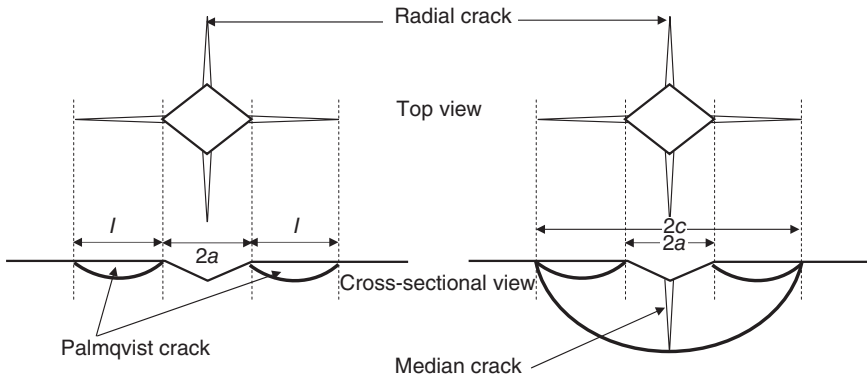
10.17 Double-cantilever beam (DCB) torsion specimen.



10.18 Tapered double-cantilever beam (DCB) specimen.



10.19 Notchless triangular prism (NTP) specimen holder and test assembly.



10.20 Indentation (Vickers) fracture toughness test.

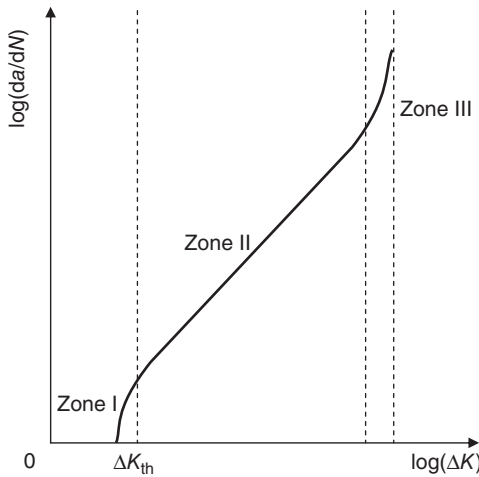
10.4 Fatigue crack propagation (FCP)

In general, a stress-based, a strain-based, or a fracture mechanics-based approach could be used to study the effect of fatigue on materials/interfaces.¹³ In a stress-based approach, a material/structure is cyclically loaded with a decreasing range of stresses and the number of cycles-to-failure is recorded for each set stress. The results are plotted in the form of $S-N$ curves in which the stress (S) to cause failure is plotted against the logarithm of the number of cycles (N) at which failure occurs.⁴⁷ The stress level at which the $S-N$ curve becomes asymptotic represents the fatigue or endurance limit of the investigated material/structure. In a strain-based approach, the cyclic stress-strain curve is analysed and a strain versus life curve is obtained.¹³

The fracture mechanics approach focuses on fatigue crack propagation (FCP), the study of crack propagation under the effect of cyclic loading.^{9,10,13,48} The presence of flaws/cracks in a material/interface suggests that a fracture mechanics approach should be used. The crack propagation behaviour of materials under fatigue loading is governed by the plane strain fracture toughness. It has been shown that K_{IC} and FCP – described by the change in crack length, a , with increasing number of fatigue cycles, N – are related through a power expression of the form:

$$FCP = \frac{da}{dN} = C(\Delta K)^m \quad [10.26]$$

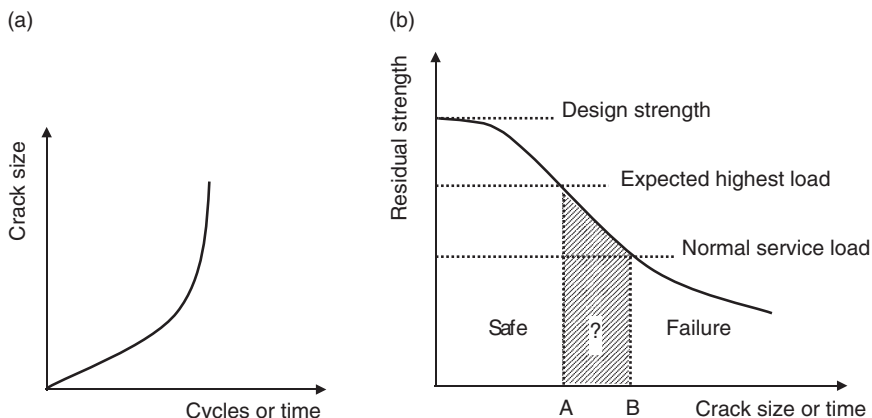
where C is a constant related to the specimen geometry, m is the slope of the log-log (with equal decades) plot of equation [10.26], and ΔK is the amplitude of the stress intensity during cyclic loading, i.e. $\Delta K = K_{I_{max}} - K_{I_{min}}$.



10.21 Log-log fatigue crack propagation rate (da/dN) versus energy release rate (ΔK).

Equation [10.26] is known as Paris' law⁴⁹ and is used to estimate the life expectancy of materials under fatigue conditions.^{9,10,13,50} For some materials, there is a threshold value of the amplitude of the stress intensity, ΔK_{th} , below which no crack growth occurs. While a log-log plot of equation [10.26] should be a straight line, in general, an 'S'-shaped curve is obtained, on which three distinct zones can be identified (Fig. 10.21). At small ΔK , beyond ΔK_{th} , the crack progresses at very low rates (zone I); this is followed by a proportional growth rate zone, where Paris' law is respected (zone II); and finally, at large ΔK , just before final failure, there is zone III where crack growth is rapid and unstable. It should be mentioned that it has been shown that K_{max} also plays an important role in crack behaviour and there have been different attempts to incorporate it in equations describing crack growth rates.¹⁰

Crack growth rates can be used for life estimates of materials/structures, as exemplified in Fig. 10.22. Figure 10.22a shows a typical plot of the crack growth rate versus the number of cycles or time. Figure 10.22b shows a graphical representation of the residual strength of a material as a function of crack size or time and identifies the design strength along with the normal and the maximum loads expected to be encountered during function. Using such an approach, one can estimate that up to point A in time or up to a size A crack, the material will be safe to use; between points A and B, the material may fail under higher than normally expected loads; and, finally, beyond point B the material is likely to fail under normally encountered loads.



10.22 a Crack size versus number of cycles or time; b residual strength versus crack size, used for lifetime predictions.

10.5 Fracture mechanics and dentistry

As early as the end of the nineteenth century, G.V. Black⁵¹ realized the importance of characterizing the mechanical properties of hard tooth tissues in order to be able to set requirements on the properties of restorative materials. Basic mechanical properties including modulus of elasticity,^{52–55} shear modulus,⁵⁶ tensile strength,⁵⁷ compressive strength,^{53,55} proportional limit,^{53,55} and Poisson's ratio⁵⁶ for both enamel and dentine have been determined. However, due to the complexity of the structures involved and the challenges raised by the small samples available, hard tooth tissues are still not fully characterized. The following sections review briefly the application of fracture mechanics to the characterization of natural hard tooth tissues, dental materials, and dental-related adhesive interfaces.

10.5.1 Enamel

Fracture mechanics and FCP methodology have not yet been applied extensively to the study of hard tooth structures and their adhesive interfaces. Rasmussen *et al.*⁵⁸ published the first report on the application of fracture mechanics methodology to the characterization of dental enamel in 1976. The authors fractured enamel specimens in a three-point bending test and, from the stress–strain curve obtained, calculated the total energy required to fracture the specimens. The total energy was then divided by the projected normal area of the two fractured surfaces to obtain what the authors refer to as the work of fracture, W_f . Enamel proved to be anisotropic with

the work of fracture being significantly affected by the orientation of enamel prisms relative to the plane of crack propagation, parallel specimens having $W_f = 13 \text{ J m}^{-2}$ while for perpendicular specimens $W_f = 200 \text{ J m}^{-2}$. In a subsequent paper, the authors showed that the results obtained were not affected by changes in temperature.⁵⁹

Hassan *et al.*⁶⁰ were the first to determine the fracture toughness of dental enamel. The determination was conducted using a microindentation technique with a Vickers' diamond indenter with 300 and 500 g loads. Fracture toughness values ranged between 0.7 and $1.27 \text{ MPa m}^{1/2}$, depending on the teeth used and the site on the tooth where the determination was performed. Anisotropy was again identified with crack propagation occurring in a direction parallel to the cervical–incisal axis, a fact attributed to the structure of enamel.

Using a microindentation technique, Xu *et al.*⁶¹ determined the fracture toughness of enamel and studied the interaction of microcracks and microstructure of enamel. The values reported, ranging between 0.44 and $1.55 \text{ MPa m}^{1/2}$, are similar to those reported by Hassan *et al.*⁶⁰ and were dependent on enamel rod orientation. Similar approaches have been used to determine the fracture toughness of enamel,^{46,62,63} the relationship between structure and fracture toughness of enamel,^{64–66} and the effect of bleaching^{67,68} and lasers⁶⁹ on the fracture toughness of enamel.

No reports have been found on the application of FCP methodology to the study of enamel.

10.5.2 Dentine

Rasmussen *et al.*^{58,59} reported the work of fracture of dentine and identified a significant anisotropy as a function of the orientation of dentinal tubules relative to the plane of crack propagation. Xu *et al.*⁶¹ were not able to determine the fracture toughness of dentine using a microindentation technique due to the absence of radial–median cracks. Marshall *et al.*⁷⁰ were also unable to determine the fracture toughness of dentine since no cracks were initiated under the experimental conditions of their nanohardness study.

A fracture toughness of $3.08 \text{ MPa m}^{1/2}$ was determined for human dentine by el Mowafy and Watts⁷¹ using the compact tension test geometry. Due to constraints regarding specimen size, the authors were not able to investigate the effect on fracture toughness of the orientation of the plane of dentinal tubules relative to the plane of crack propagation.

The determination of fracture toughness of human dentine and the study of the effect of the orientation of the plane of dentinal tubules relative to the plane of crack propagation have been reported.^{72,73} Three orientations were tested: (a) the plane of crack propagation perpendicular (PE) to

the plane of dentinal tubules; (b) the plane of crack propagation parallel and aligned (PAA) to the plane of dentinal tubules; and (c) the plane of crack propagation parallel and transverse (PAT) to the plane of dentinal tubules. A significant anisotropy of dentine in relation to its fracture toughness has been identified with fracture toughness values of $\sim 2 \text{ MPa m}^{1/2}$ in both the PAA and PAT directions and $\sim 1 \text{ MPa m}^{1/2}$ in the PE direction. The identified anisotropy is in accordance with the work of fracture results published by Rasmussen.^{58,59} It is interesting to note that Kinney *et al.*⁷⁴ concluded, based on an atomic force microscopy (AFM) indentation study, that tubule orientation had no effect on the elastic behaviour of normal dentine. The same authors, however, identified significant differences between peritubular and intertubular dentine with respect to their elastic moduli and hardness. The determination of the fracture toughness of dentine has been the focus of other reports as well.^{75,76}

Several research groups have undertaken the FCP characterization of dentine^{22,37,77–89} showing that fatigue resistance is influenced by the orientation of dentinal tubules,⁸⁰ is affected by the environment,^{87,88} and demonstrates an *R*-resistance type curve.⁸⁵ Kruzic and Ritchie⁹⁰ have suggested that the application of the Kitagawa–Takahashi diagram could generate quantitative predictions of the conditions, in terms of applied stress and flaw size, for fatigue failure in human dentine.

10.5.3 Dentino-enamel junction

The dentino-enamel junction (DEJ) has received considerable interest due to both its unique structure and the fact that there has been some discussion regarding its ability to stop/deflect cracks originating in enamel. Rasmussen determined an average work of fracture of 336 J m^{-2} for the DEJ.⁹¹ The author speculated that the dentine in the proximity of the DEJ is more resistant to failure than dentine farther from it. Marshall *et al.*⁷⁰ reported difficulties in initiating cracks that would traverse the DEJ. They were, however, able to monitor the change in elastic modulus and hardness across the DEJ using nanohardness testing.

Lin and Douglas,⁹² using a chevron-notched short bar configuration, studied the crack propagation through enamel and dentine in a plane perpendicular to the DEJ. A fracture toughness value of $3.38 \text{ MPa m}^{1/2}$ and a corresponding strain energy release rate of 988.42 J m^{-2} were determined. The authors identified a significant plastic deformation that occurred at the DEJ. The fracture mechanics tests were correlated with fractographic characterizations and previous scanning electron microscopic studies of the DEJ.⁹³

The ability of the DEJ to deflect the FCP path as cracks propagated across it was demonstrated by Dong and Ruse.⁴² Results of fracture mechanics investigations of the DEJ were also reported by others, highlighting the critical role of the DEJ in protecting the integrity of the tooth structure through crack deflection/crack arrest.^{83,94} Understanding the mechanism of crack deflection could help in improving dentine–composite as well as ceramic–cement interfacial qualities with the aim of decreasing the risk of clinical failure of restorations. A modified cantilever beam was used to assess the toughness (G_c) of the cementum–enamel junction in equine and bovine teeth identifying the crack bridging mechanism responsible for the higher toughness of equine teeth.⁹⁵

10.5.4 Dental resin composites

Following the pioneering work of Lloyd in the 1980s,^{96–100} others have used a fracture mechanics approach to characterize dental resin composites.^{30,40,101–121} Over the last several years, reviewing the relevance of materials testing for the clinical performance of resin composites, it has been recommended to include fracture toughness and fatigue tests.^{122,123} Recognizing the importance of and the increased interest in the fracture mechanics characteristics of composites, even dental manufacturers have started lately to list K_{IC} values for their marketed composites.

While there are several papers on the fatigue behaviour of dental resin composites (such as references 124–127), or on the effect of aging on their fracture toughness,¹²⁸ no reports have been found on the application of FCP methodology to their study.

10.5.5 Enamel–composite interface

Rasmussen¹²⁹ first reported the application of fracture mechanics methodology to the study of the enamel–resin composite adhesive interface. The author determined a work of fracture of 61 J m^{-2} (range $34\text{--}130 \text{ J m}^{-2}$) and observed that failure consisted more of broken deep resin tags rather than an interfacial failure. Twelve years later, de Groot *et al.*¹³⁰ set out to determine the enamel–resin composite interfacial K_{IC} and the J integral using a single-edge-notched specimen loaded in three-point bending. The K_{IC} values determined ranged between 0.8 and $2.18 \text{ MPa m}^{1/2}$ and were influenced by the material used and the type of failure initiation (enamel, composite, interface).

No other studies have been found on the application of fracture mechanics methodology to the study of enamel–resin composite adhesive interfaces. No reports have been found on the application of FCP methodology to the study of the enamel–resin composite adhesive interface.

As far as this author is aware, there have been only three papers published on the fatigue behaviour of enamel–resin composite adhesive interfaces.^{131–133}

10.5.6 Dentine–composite interface

The dentine–resin composite adhesive interface has been investigated using fracture mechanics methodology, a methodology that has been recommended over traditionally used shear bond strength tests.^{134,135} The notchless triangular prism specimen fracture toughness test was specifically developed for the application of fracture mechanics methodology to the study of adhesive interfaces.^{44,136–140} During the same time period, two other research teams applied fracture mechanics methodology based on the chevron-notched short rod specimen to the characterization of dentine–resin composite adhesive interfaces.^{141,142} Armstrong *et al.*,^{143,144} Toparli and Aksoy,¹⁴⁵ and Ryan *et al.*¹⁴⁶ used similar fracture mechanics approaches to characterize adhesive interfaces involving dentine. The fracture mechanics approach enabled researchers to better characterize the failure mechanism,¹⁴⁷ to study the effect of dentine surface preparation,¹⁴⁸ dentine depth,¹⁴⁹ and interface stiffness¹⁵⁰ on interfacial fracture toughness. A mixed mode, chevron-notched, interfacial fracture toughness test has also been proposed to investigate the mixed-mode fracture of dentine–composite interfaces.^{151,152}

No reports have been found on the application of FCP methodology to the study of the dentine–resin composite interface.

10.5.7 Dental cements

The fracture toughness of many commercially available dental cements has been determined using different sample configurations: compact tension,^{21,153} single-edge-notched beam in three-^{154,155} and four-¹⁵⁶ point bending, short rod chevron-notched,^{23,26} ring-shaped,¹⁵⁷ double-torsion,^{158–161} and notchless triangular prism.^{138,162,163} The results obtained range from 0.12 MPa m^{1/2} for zinc phosphate cements, to over 2 MPa m^{1/2} for adhesive resin cements (Super Bond, Sun Medical, Japan)¹³⁸ and they highlight the significant improvement of resin-modified glass ionomer cements (0.8–0.9 MPa m^{1/2}) over glass ionomer cements (0.3–0.6 MPa m^{1/2}).^{23,153,157,161}

10.5.8 Dental ceramics

Indentation fracture toughness,^{46,164–166} single-edge-notched beam specimen fracture toughness test,^{28,167,168} and fractographic characterization^{169–172} are the most prevalent fracture mechanics methodologies used in the study of

dental ceramics and they have been extensively applied. The values reported range from $\sim 1\text{--}1.4\text{ MPa m}^{1/2}$ for feldspathic porcelains to $8\text{--}10\text{ MPa m}^{1/2}$ for zirconia-based ceramics.

10.5.9 Denture base materials

Fracture mechanics methodology has been applied to the determination of fracture toughness of denture base materials using single-edge-notched specimens^{32,41,173} and tapered double-cantilever beams.⁴¹ Fracture toughness determinations enabled a better demonstration of the effects of resin modifications than impact tests¹⁷³ while the double-cantilever beam tests provided a more precise view of the fracture process.⁴¹

10.6 Summary

In this chapter, an attempt has been made to present a succinct but comprehensive review of the application of fracture mechanics methodology in the characterization of hard tooth tissues, dental materials, and dentally related adhesive interfaces. The references provided should enable interested researchers to retrieve information regarding test methodologies, sample parameters, and results obtained. It is hypothesized that results of fracture crack propagation studies will provide better predictors for the *in vivo* performance of restorative materials and restored teeth. Fracture mechanics investigations could lead to the optimization of not only the structure of materials and interfaces but also of the design of restorations. It is quite encouraging to notice the significant increase in the number of papers using fracture mechanics methodologies and the number of young researchers involved in the field.

10.7 References

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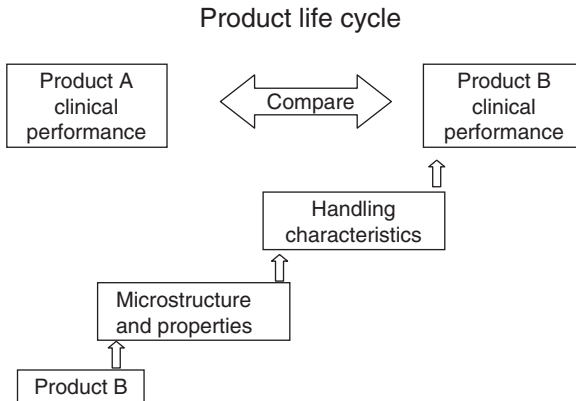
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11.1 Introduction

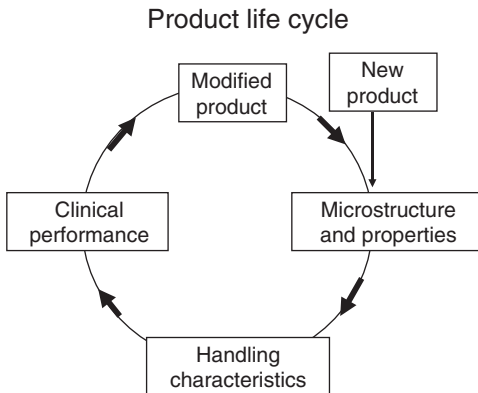
A considerable number of years ago, when I first joined the Dental School in Sheffield, I raised the question as to which was the best resin composite on the market. The only feedback I could get at the time was some comments about the relative merits of different materials based on personal experience and personal interpretation of a limited array of laboratory data about the products then on the market. In my naivety it seemed that a clinical study should be able to answer that question without too much difficulty. Ten years later I realized that things were not quite as straightforward as I imagined. By the time the work was published (van Noort and Davis, 1993), most of the materials that had been selected for the study no longer existed and thus although it answered the fundamental question as to which material was best, the question itself had become irrelevant.

The presumption with an evidence-based approach to the selection of dental materials is that a material is developed and tried clinically and in time we receive feedback on its clinical performance. In the meantime, a new material comes along and as we receive clinical feedback on its performance we can then compare one with the other material and decide which is the better of the two (Fig. 11.1) (see www.cebm.utoronto.ca). In reality the life span of a dental material is probably no more than 3–4 years before it is modified in the light of clinical experience and with each change the gathering of an evidence base of performance has to start all over again (Fig. 11.2). The extrapolation of data from one material to its supposed improved version is fraught with danger and the path to better dental materials is littered with casualties where the new improved version did not live up to expectation. Thus, by the time we have the clinical data it is too late to use it in our decision making as the material has changed or disappeared from the market.

My reason for recounting this story is that as a consequence of the short life span of a dental material, enormous emphasis is placed on the proper-



11.1 The product life cycle as often assumed in definitions of evidence-based medicine.



11.2 The product life cycle of a dental material as it goes through repeated numbers of iterations.

ties of a dental material that can be measured in the research laboratory as the gathering of clinical evidence takes such a long time. Thus, the collection of laboratory data is often perceived as being driven by a desire to use such data as a predictor of clinical performance. It is important that this point is appreciated from the outset as this puts quite a different complexion on the reasons why many laboratory-based experiments are carried out on dental materials. Whereas the research of the clinically oriented scientist seeks to establish a link between experiments carried out in the laboratory and the potential clinical performance of a material, the materials scientist's view of laboratory experiments is, generally speaking, quite different from this. The materials scientist will carry out experiments in the laboratory in order

to understand how a material behaves and what factors control its behaviour. This allows the scientist to identify ways and means of improving the properties of a material. From their perspective, whether or not the material will meet the needs of a certain application may only be a secondary consideration. For example, the laboratory-based scientists may improve the properties of a fibre-reinforced resin composite but they would not even attempt to claim that this would make the 'improved' material suitable for making dentures or dental bridges. The point I am seeking to make is that some experiments are designed to test the fundamental behavioural characteristics of a material and other experiments are designed to study their performance when in function. It is important that we differentiate between these two types of experiments. For example, a micro-tensile bond strength test is designed to assess the fundamental behavioural characteristics of materials, whereas a microleakage test examines the performance of a material during function. The latter can generally be regarded as an attempt to test the material in a situation that simulates the clinical application of the material. One distinct difference between the two approaches is that, in the former, the variables can be reasonably carefully controlled, whereas in the case of the latter one has to deal with a multitude of variables that contribute to the outcome.

In this chapter, the various approaches to the laboratory-based assessment of dental adhesives will be explored. We will take a critical look at the design of the experimental methods and clarify issues in relation to our ability to assess the performance of an adhesive.

11.2 Rationale for bond strength testing

It is not unreasonable to take the point of view that if a material is to be used as an adhesive then one should test its adhesive qualities. However, that does not necessarily mean that we only need to look at the ability of the adhesive to bond to a surface, be it soft tissue, bone, enamel, dentine or any man-made material. One factor that is often overlooked is the requirement for the adhesive to act as a means of transferring load from one part of a structure to another. This generates stresses and strains within the adhesive and it is important that the adhesive has the necessary mechanical properties to withstand these stresses and strains. For example, one might happily use Blu-Tack to stick bits of paper to the wall but one wouldn't do the same with a framed picture. The ability of the Blu-Tack to stick to the wall or the picture is not really the issue here, but its inability to carry load is a problem and is fundamentally the reason why it would fail as an adhesive. Thus, the assessment of an adhesive should be based not merely on its ability to stick but also its ability to carry load; that is, more often than not, the adhesive has to be able to contribute to the structural integrity of the

whole unit. This requires one to differentiate carefully between the need to assess the integrity of an adhesive bond on the one hand and the requirement for a structure to carry load on the other. Some experiments are designed to do the former, while others are designed to test the latter. Those designed to test structural integrity can be recognized as experiments that seek to simulate the clinical situation. Thus shear or micro-tensile bond strength tests are experiments that test the integrity of the adhesive bond, while the enamel debonding test for an orthodontic bracket is an experiment seeking to simulate the clinical situation.

When one sets out to design a research project, the starting point is always to define the question one is seeking to address. Once one knows the question to ask one can then design the experiment that will seek to answer that question. This may all seem very obvious but it is noticeable in the ways that data are manipulated and presented that this fundamental point is often overlooked. When one considers this in the context of bond strength testing then it is important to appreciate that most bond strength tests are designed and conducted to answer a specific question. For example, a bond strength experiment may be conducted to determine the quality of the adhesion of a particular bonding system by examining the bond strength, and perhaps more importantly the mode of failure. Based on the information obtained it may be possible to suggest a means of improving the adhesion by overcoming any weaknesses that have been identified. You will note that this experiment would not provide an answer as to the clinical performance of the adhesive since that wasn't the question that was addressed. Nevertheless we regularly see attempts to try to extrapolate from bond strength data to clinical performance. If one wants to ask the question: 'What is the relationship between bond strength and clinical performance?', then one must design quite a different experiment to answer that question. Conducting only bond strength tests will not answer that question. Thus, it needs to be made clear from the outset what is the purpose of the experiment being conducted. In summary, one can look upon adhesive interface testing as addressing different issues depending on how the experiment is designed. It is vitally important that the experiment undertaken matches the question asked such that one does not fall into the trap of making unjustified extrapolations to situations that the original question was not meant to address and for which the experiment was not designed.

11.3 Classification of dental adhesive testing techniques

The types of laboratory experiments that can be conducted on dental adhesives can be classified into two types, namely behavioural tests and structural integrity tests. In the behavioural tests one seeks to establish the

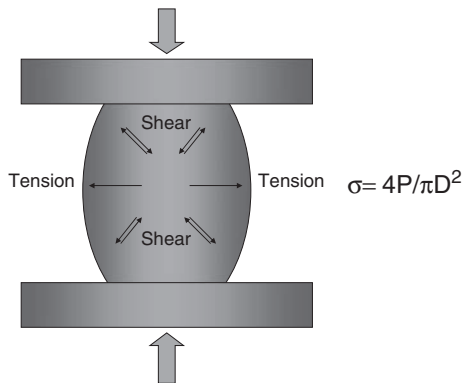
fundamental material behavioural properties. Examples of the sorts of things one might measure are tensile strength, elastic modulus, fracture toughness, coefficient of thermal expansion and translucency. In structural integrity tests, one sets out to provide an experimental arrangement that simulates the usage of the materials. Typical examples of such tests in dentistry include strength and fatigue testing of crowns and bridges, wear tests and microleakage tests. It is important to appreciate the distinction between these two approaches to materials testing.

11.3.1 Behavioural tests

In the behavioural tests the focus is on understanding how the material behaves and how one might be able to change the properties of the material by changing such things as its composition. The critical feature of the design of these experiments is that one needs to ensure that the data gathered are correct and appropriate, otherwise they can very easily be misinterpreted and the wrong conclusion may be drawn. For example, in the compressive strength test of a cylinder, the failure of the materials is in fact a combination of shear and tension, and the calculation of the compressive strength by dividing the stress at failure by the cross-sectional area of the cylinder is actually not valid (Fig. 11.3).

If one simply uses the test as a means of monitoring the setting process over time of a material such as a glass ionomer cement, or monitoring whether the compressive strength of the material is improved or made worse by a change in formulation, this does not matter, but if one were to

Compressive strength test



11.3 Complex tensile and shear stresses generated in a compressive strength test; σ , stress; P , load; D , diameter.

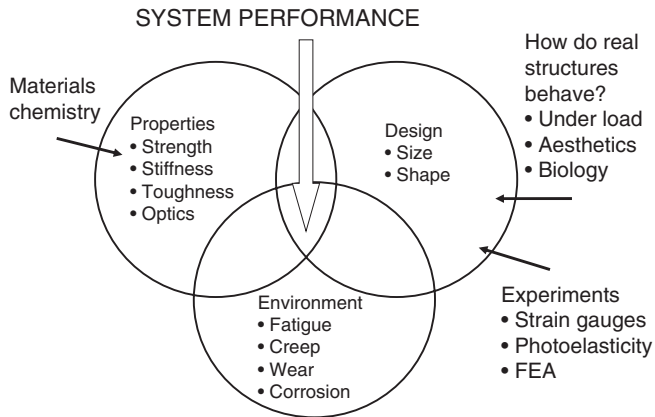
try to extrapolate the data from the compressive strength test to a clinical compressive loading situation then this would be an erroneous use of this property of the material, since the stresses and strains generated under clinical loading conditions will be quite different from those in a compressive strength test.

11.3.2 Structural integrity tests

In structural integrity tests, the material is being applied in a situation in an attempt to provide some insight into how the material might respond to a clinical environment and to learn what makes the structure fail. This will be a complex interaction between material, design and environment. Thus, the structural integrity test is seeking to establish a link between the material and its performance in a clinical situation. How effective this is depends on the quality of the design of the structural integrity test and there will be a need to validate the simulation.

The testing of crowns and bridges under various loading conditions is an example of structural integrity testing. Some of these tests are designed to answer the question as to whether or not the structural integrity is compromised by a change in materials or design, of which a typical example is the so-called ‘crunch the crown’ experiment. Often such experiments are criticized for their lack of clinical relevance, but one has to remember that these experiments are designed to assess the complex interaction between materials and design. The question being addressed in such experiments is whether or not the structural integrity of the structure has been compromised to such a degree that there is little point in carrying out the much more complex and time-demanding experiments that test the durability of the structure. If one now adds the ingredient of environment along with those of materials and design, then the experimental design needs to reflect that and issues such as cyclic loading and corrosion become much more important (Fig. 11.4). One sees this for example in wear tests, which try to examine simultaneously the complex interaction between different loading conditions and environments, and where the validity of the clinical wear simulation will determine the popularity of the wear tester in terms of its ability to predict the clinical performance of a material or a device.

As the experimental design becomes more concerned with asking questions about the potential performance in the clinical situation, so the experiments make a paradigm shift from the evaluation of the physical and behavioural characteristics of materials to what is more accurately described as system performance. It is important that this distinction is appreciated, otherwise one may fall into the trap of thinking that one is undertaking a test to determine fundamental materials properties whereas in fact one is



11.4 The factors influencing the performance of dental materials in the oral environment. (FEA, finite element analysis.)

conducting a structural integrity test. For example, the testing of the bond strength of orthodontic brackets is a structural integrity test, not a test of behavioural characteristics, and is potentially open to misunderstanding if one is unaware of this distinction (Eliades and Brantley, 2000).

It is important that the distinction between a behavioural test and a structural integrity test does not become blurred as the danger is that the experiment will not be able to provide valuable answers. Thus, the focus in the behavioural test must be on ensuring that the measurements undertaken provide genuine and reliable information on the behavioural characteristics of the material, while the structural integrity test must be so designed to provide a worthwhile simulation of the structure to be tested.

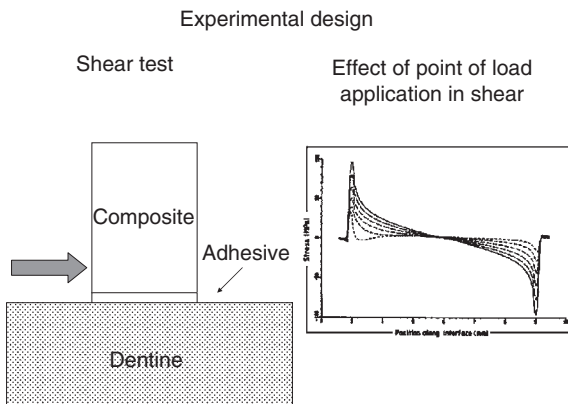
11.4 Behavioural adhesive tests

Next, I will explore some examples of what I consider to be behavioural tests and address some of the issues that arise in relation to how these tests are designed and conducted. However, before proceeding it is worth reiterating that in my view these experiments are not designed to assess the clinical performance of the materials used. Thus, it is pointless to enter into a discussion as to the clinical relevance of these experiments. What is important is that the experiments are designed such that the information obtained can be understood and is open to the correct interpretation. The focus of this discussion will be the methods used to assess the quality of adhesion between dentine and resins, although there are obviously other examples of fundamental tests of adhesion such as bone bonding to implants (Lin

and Yen, 2004), resin bonding to fibre posts (Ferrari *et al.*, 2006) or resin bonding to ceramics (Kern and Wegner, 1998; Della Bona *et al.*, 2000).

11.4.1 Shear bond strength test

Of all the adhesive tests used in dentistry, the shear bond strength test has been one of the most popular bonding experiments ever devised. Its popularity has much to do with the simplicity with which this experiment can be conducted. When this experimental design was first introduced the quality of the dentine bonding agents was quite poor relative to the bonding agents available today. In those initial experiments the bond strength was so poor that failure would generally occur at the adhesive interface such that the bond strength, reported as a shear stress based on the ratio of load to bonding area, could be used as a measure of the quality of the adhesion achieved. As the quality of the adhesive bond improved then one would expect this to be reflected in an increase in the shear bond strength. However, it should be noted that this calculation of failure stress is in fact erroneous. The experimental design of the specimen and the manner of loading are such that the stresses experienced at the adhesive interface are extremely complex, as shown in Fig. 11.5. Failure is more likely to be due to interfacial tensile stresses generated as a consequence of the bending action rather than genuine shear (van Noort *et al.*, 1989). In addition, these tensile stresses can be considerably higher than the calculated shear stress. When bond strength values were low this was not a problem and as long as the experi-



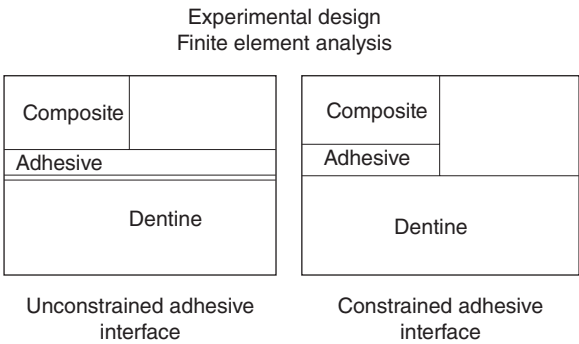
11.5 Interfacial stress distribution of the vertical stresses (σ_{yy}) for a shear bond strength test arrangement, showing high levels of tensile stress below the point of load application and compressive stresses on the side opposite to the point of load application.

mental design used was consistent in terms of size, shape and load application, different adhesives could be compared by calculating the nominal shear bond strength.

Where one has to be really careful is in comparing shear bond strength data from experiments carried out in different laboratories. Minor modifications in the method used can potentially have a profound influence on the outcome of the experiment, such as, for example, the mode of application of the adhesive. Quite different results can be obtained if the adhesive is applied liberally over the dentine surface as compared with when it is constrained to the adhesive interface (van Noort *et al.*, 1991). This problem is exacerbated by all the other variables that can come into play when bonding to dentine (Al-Salehi and Burke, 1997; Tay and Pashley, 2004).

Figure 11.6 shows that, for the unconstrained adhesive interface situation, the maximum stresses tend to occur at the adhesive/composite interface, while for the constrained condition the maximum stresses are at the dentine/adhesive interface, which invariably will produce different results. Thus, while it is reasonable to compare the adhesive performance of different dentine bonding agents within a laboratory, the comparison of data from different laboratories is fraught with danger, unless one can be sure that exactly the same experimental conditions were used.

As dentine bonding agents improved so another problem came to light, namely fractures no longer occurred at the adhesive interface but would tend to be cohesive in nature, more often than not involving the dentine. The reason for this is that the stresses generated by the bending action will predispose any crack that forms to deviate into the dentine when confronted with a strong adhesive bond. In shear bond strength tests this deviation of the fracture mode from the interface into the dentine tends to occur



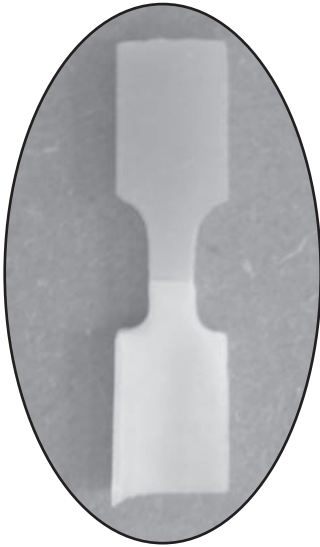
11.6 Finite element analysis of the stress distribution for an unconstrained adhesive interface and a constrained adhesive interface.

at a nominal shear stress of some 20 MPa. This has led some people to suggest that the bond strength exceeds the cohesive strength of the dentine and that the maximum bond strength that can be achieved to dentine is of the order of 20 MPa, which seriously misunderstands the actual situation. This interpretation does not fit comfortably with the observation that the ultimate tensile strength of dentine may be as high as 100 MPa (Bouillaget *et al.*, 2001). It is much more likely that the transition from an interfacial failure to a cohesive failure of the dentine is as much a consequence of the improved adhesion as it is of the design of the experiment. A similar problem arises with shear bond strength testing of resins to ceramics, where fractures are frequently cohesive in the ceramic (Blatz *et al.*, 2004), which has been shown to be an experimental artefact (Della Bona and van Noort, 1995). The correct way to interpret the situation is that when cohesive failure of the dentine becomes the dominant mode of failure, it is no longer possible to differentiate between the different dentine bonding agents and an alternative test needs to be used. One such test that is gaining in popularity is the micro-tensile bond strength test.

11.4.2 Micro-tensile bond strength

The micro-tensile bond strength test has been gaining in popularity since it was first introduced in the early 1990s (van Meerbeek *et al.*, 2003). The most important difference between the micro-tensile test design and the shear test design is the potential ability for the micro-tensile bond strength test to be able to calculate the average tensile stress at the adhesive interface. The concept is the same as one that has been used in engineering for decades whereby the stress strain behaviour of a material is assessed using a dumbbell specimen design (Fig. 11.7). The idea behind this design is that all measurements are taken in the central part of the specimen, well away from the clamping site, such that a uniform stress field is generated and the local tensile stress can be calculated simply from the load divided by the cross-sectional area. The wider section of the specimen at each end is there to ensure that the specimen could be easily gripped and to avoid failure within the clamping zone as this would invalidate the experiment.

What this means is that it is then possible to assess the quality of the adhesion by comparing the tensile stress at failure for different bonding agents, evaluate the mode of failure and maybe identify the weakest link in the system, without this being influenced by geometric design features. The two notable differences that should strike one immediately when examining micro-tensile bond strength data: firstly, the 20 MPa ceiling observed for the shear bond strength test has disappeared and tensile bond strengths in excess of 40 MPa can be achieved; secondly, cohesive failure of



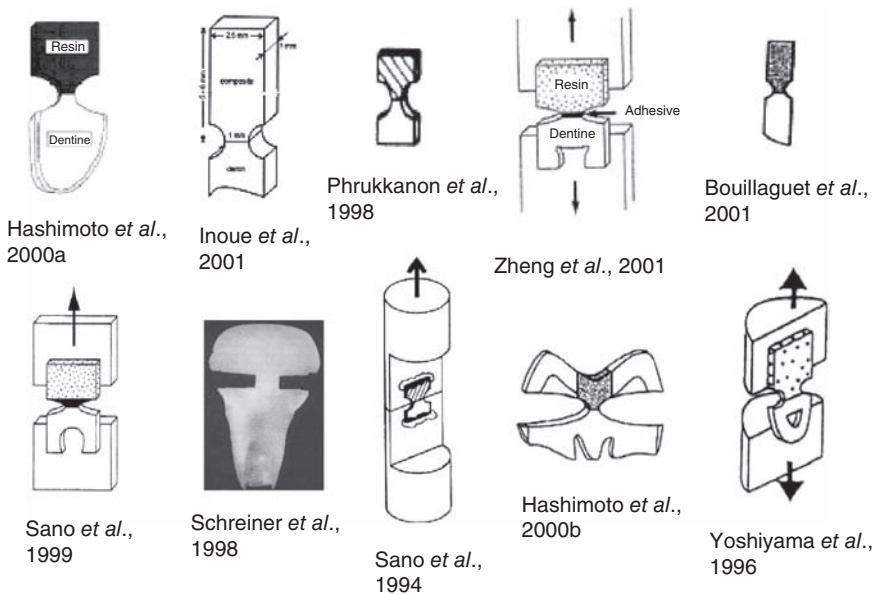
11.7 Dumbbell specimen design.

the dentine is a much less common occurrence. Thus, the constraints imposed by the design of the shear bond strength test have been removed.

As with all new tests, within a very short time of its introduction, various forms of the micro-tensile bond strength test have appeared (Fig. 11.8). There is a danger with these alternative designs that the original premise of producing a uniform stress at the interface is lost. The sorts of designs now used include the simple stick, dumbbell and various re-entrant designs. It is the latter that have become the main area of concern, since the interfacial stress will be affected by the degree of the re-entrant design. This means that we could again find ourselves in the situation where it becomes impossible to compare the results from different laboratories because of the use of different specimen designs.

Recently published work has shown that the micro-tensile bonds strength for the stick, dumbbell and parabolic designs are pretty much the same, but that sharp re-entrant shapes underestimate the stress at failure due to the stress-concentrating effect of such designs, which would suggest that one might as well use the stick specimen design since it is the easiest to produce (Betamar *et al.*, 2007a, 2007b).

However, using the same design is not yet the complete answer to producing results that can be compared from one laboratory to another. There is also the issue of size and results will not be comparable if widely different specimen sizes are used, despite them having the same shape. Since the days of Griffith's experiment on glass fibres it has been known that smaller



11.8 Various designs used in micro-tensile bond strength tests.

specimens are stronger and that this is simply a consequence of the reduction and removal of inherent flaws in the system (Gordon, 1968). The same applies to the specimens used in the micro-tensile bond strength tests and a valid comparison is only possible if specimens are of a similar size or, better still, of the same cross-sectional area (Sano *et al.*, 1994).

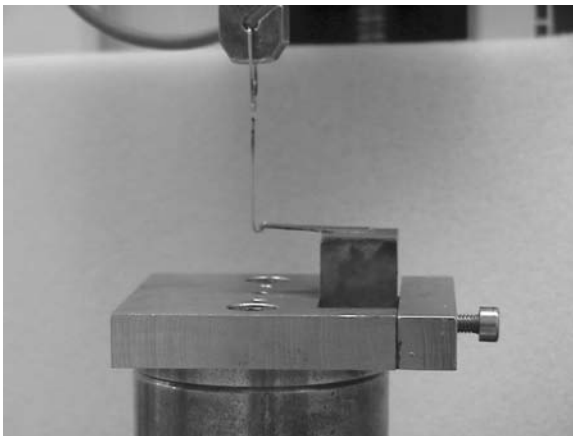
11.5 Structural adhesive tests

It is important to appreciate the distinction between a behavioural adhesive test as described above and a structural adhesive test. Whenever a dental device is used in an experimental design that mimics its use clinically this is a structural integrity test. For example, pull-out tests for fibre posts (Giachetti *et al.*, 2004), debonding of orthodontic brackets (Vicente *et al.*, 2006), debonding of resin-bonded bridges (van Dalen *et al.*, 2005) and crown retention tests (Palacios *et al.*, 2006) are all structural integrity tests. The experiment involves the testing of the whole system and thus one is looking at a system response. A consequence of this is that it generally turns into a multi-factorial problem that needs very careful analysis. If appropriately constructed in terms of the question the test is trying to address then such tests can be very enlightening. One obvious concern with structural integrity tests is the validity of the experimental design used and its ability to answer the question it is seeking to address.

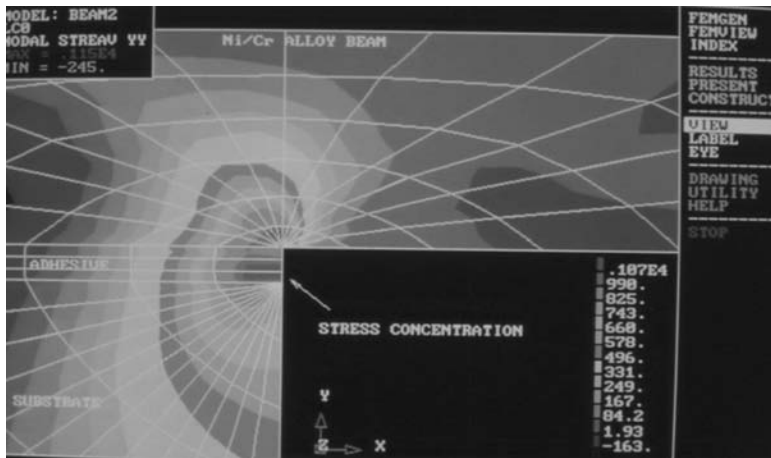
11.5.1 Structural integrity tests for cantilever resin-bonded bridges

As an illustration of how a structural integrity test can be used to acquire useful information on the behaviour of a complex system, I would like to take a closer look at the cantilever resin-bonded minimum preparation bridge. Numerous shear and tensile bond strength tests have been conducted with bond strengths typically being in the region of 30–40 MPa. This would suggest that a debonding force of some 300–700 N would be required to debond a cantilever resin-bonded bridge if based simply on the area of bonding provided, which obviously is absurd (van Noort, 2005). Thus it was proposed that a peel test along the lines shown in Fig. 11.9 would be more realistic for the assessment of the adhesion of the bridge.

The debonding force for the beams was found to be no more than 25 N in this experimental design, which is considerably more realistic (Northeast *et al.*, 1994). Perhaps this is not surprising since the design produces a highly significant stress concentration at the point where the beam attaches to the base, as shown in the finite element analysis (FEA) of the system in Fig. 11.10. One concern in such a test is always whether or not the correct loading condition has been considered. Further experiments were conducted to assess the failure load in what would be the occlusal direction and it was found that the failure loads for occlusal loading were some seven times higher than those for the peeling condition (Bhakta *et al.*, 2006). Similar observations have been reported by van Dalen *et al.*, (2005) and thus it is reasonable to assume that failure is most likely to occur by a peeling action.



11.9 Design of a simple peel test for a cantilever bridge.



11.10 FEA model of the local stress distribution for the vertical tensile stress (σ_{yy}) for a cantilever beam.

Table 11.1 Effect of elastic modulus on the maximum stress for the peel test arrangement

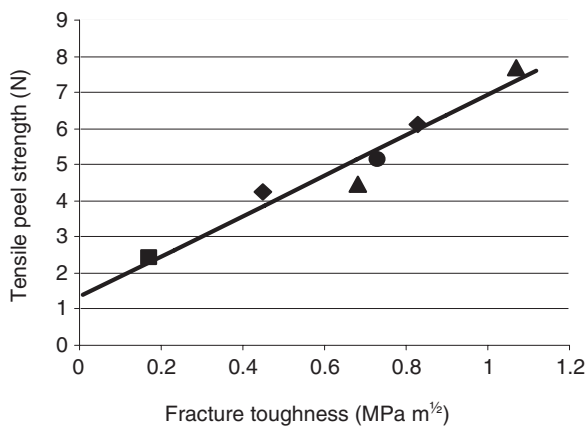
Material	Elastic modulus (GPa)	Maximum σ_{yy} (MPa)
Adhesive	10	74
	5	54
	1	30
Beam	200	54
	100	75

The benefit of combining the experimental work with FEA modelling is that it provides an opportunity to interrogate the system and get an idea of what would happen if certain parameters were changed. For example, one can change the elastic modulus of the adhesive or the beam and see how this influences the peak stress in the system. The results for such an analysis are shown in Table 11.1, which would indicate that a combination of a high-stiffness beam material and a low-stiffness adhesive would provide the best outcome. This idea that a low elastic modulus adhesive provides a better resistance to failure by peeling forces deserves further study, especially since this fundamental material property has not previously been considered as a parameter for the selection of a resin-bonded bridge adhesive.

Another material parameter that may have an influence on the outcome is the fracture toughness of the adhesive, which is based on the observation

that the fracture is initiated in the adhesive. As it happens, Knobloch *et al.* (2000) had carried out a series of experiments on the fracture toughness of luting agents and so this afforded us the opportunity to compare the peel strength of these adhesives with their fracture toughness. The results of this comparison are shown in Fig. 11.11 and there appears to be a very close correlation between fracture toughness and peel strength (Al-Ghananeem and van Noort, 2004). This would suggest that a combination of low elastic modulus and high fracture toughness is required for an adhesive for cantilever resin-bonded bridges. Thus, it may be possible to link the material's fundamental behavioural properties to those of the system and point us to a possible solution to a problem.

An alternative approach that can help to improve the performance of the system is to consider a change in design. The fundamental weakness is the stress concentration that arises at the point of attachment of the tooth. One way of dealing with this is to change the position of the attachment, as shown in the clinical case study in Fig. 11.12. A comparison of the peel force between the cantilever and lingual bar designs showed a peel force for the old design of 7N as compared with 38N for the new design (Bhakta *et al.*, 2006). There is no doubt that there are potential problems with the proposed design, but the important point that I wish to illustrate with this example is that sometimes we need to take a step back and consider the whole system and how we may change its behaviour rather than focusing on the materials that make up that system.



11.11 The relationship between tensile peel strength and fracture toughness of a range of luting agents.



11.12 Suggested alternative design for a cantilever resin-bonded bridge.

11.6 Future trends

It seems to me that there are a number of avenues that still need to be trodden before we can make the connection with clinical performance. With regard to the assessment of the fundamental behavioural properties of adhesive interfaces, there is more we can do. In the case of dentine bonding, with the micro-tensile bond strength test we have an effective means of assessment of the tensile bond strength of resins to enamel and dentine and the technique can be applied to a variety of other materials. However, it is generally accepted that failure in shear occurs at lower stresses than failure in tension and therefore we could do with a shear bond strength test that genuinely assesses the resistance of the adhesive interface to shear stresses and would be as widely accepted as the micro-tensile bond strength test. Perhaps the push-out test deserves closer examination (Dhert *et al.*, 1992) or some form of torsional shear test. Also a fracture mechanics approach to the assessment of adhesive interfaces can potentially provide more insight (Lin and Douglas, 1994; Tantbirojn *et al.*, 2000; Armstrong *et al.*, 2001; Della Bona *et al.*, 2006).

Another aspect of the performance of dental adhesives that requires more attention is the durability of the bond under the aggressive conditions of the oral environment. This could range from examining the effects of long-term storage in water, or perhaps some more aggressive medium such as artificial saliva, in order to test hydrolytic stability (Carrilho *et al.*, 2005; De Munck *et al.*, 2006), to cyclic fatigue loading of the interface (Attia and Kern, 2004; De Munck *et al.*, 2005).

Structural integrity tests can play an important role in the identification of potential weaknesses in a system. However, by their nature such tests

are more complex and thus the results are generally speaking more difficult to interpret and also more prone to misinterpretation. Thus, it is important that these tests are designed in such a way as to be able to address the question that is being asked, and no more or no less.

Alongside the experimental testing of the structural integrity of a system, computational modelling of the system is gaining more popularity, be it an implant replacing a missing tooth (Pilliar *et al.*, 2006), an orthodontic bracket (Katona, 1997), a veneer (Magne and Douglas, 1999) or a filling (Borkowski *et al.*, 2006). One can approach this from the concept of benign design, by which I mean how the interfacial stresses can be minimized (Richardson *et al.*, 2001; Bhakta *et al.*, 2006). This is hard enough and an even greater challenge is to try to link the data from behavioural tests, such as the micro-tensile bond strength test, to the interfacial behaviour of a bonded structure under load (Fennis *et al.*, 2005). This would provide us with the potential to make a prediction as to where and at what load an adhesive interface in a dental structure, such as a restored tooth, will fail and what we may have to do to prevent this from happening. If that were possible then we would have a seamless transition of understanding from the fundamental laboratory test to the clinical performance of our dental adhesives and we would begin to bridge the gap between dental engineering and the other engineering disciplines.

11.7 Summary

We have a challenge to develop behavioural and structural tests for dental adhesives that are relevant to their clinical application (van Meerbeek *et al.*, 2003). If we are prepared to accept that our starting point is to use such tests to understand better how the materials we use and the structures we create work in practice, then such understanding and knowledge can be used to improve the system behaviour. In due course we may begin to move closer to the goal of being able to carry out laboratory-based experiments that will inform the clinical performance of the materials and systems being evaluated.

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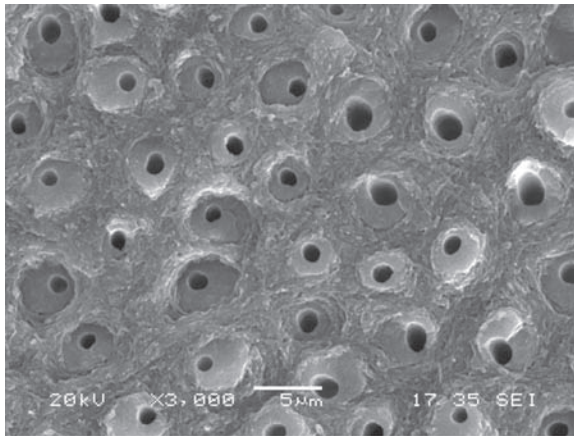
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12.1 Introduction

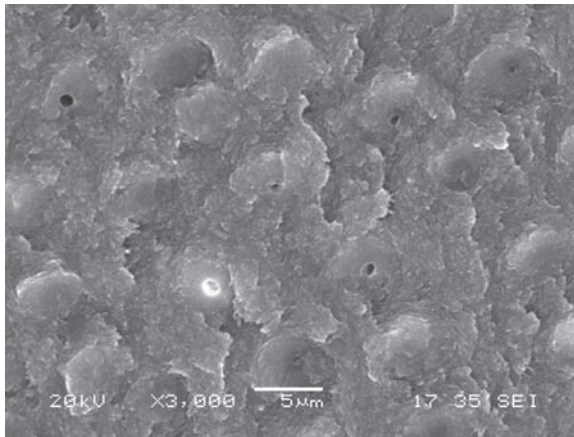
Due to a number of advances in dentistry over the past few decades, the number of partially and/or fully dentate seniors is steadily increasing. With this growth in senior patients there are new challenges. Seniors are seeking restorative care more frequently and are at a greater risk of suffering from recurrent decay and other forms of restorative failure (Chiappelli *et al.*, 2002). Nearly 40% of all restorations are placed in patients over 50 (ADA, 2002), and tooth fracture is most common in seniors (Ellis *et al.*, 1999; Ratcliff *et al.*, 2001; Wahl *et al.*, 2004). The greater incidence of tooth fracture in these patients could simply arise from the prolonged period of oral function, or from changes in the structural behavior of dentine and enamel with aging.

From a materials perspective, changes in the mechanical properties of dentine with aging are not unexpected. Dentine exhibits a relatively complex hierarchical structure (Kinney *et al.*, 2003) and is comprised of both organic and inorganic components. The dentine tubules exist as a network of microscopic channels that extend radially outward from the pulp towards the dentine–enamel junction (DEJ) and cementum. The tubule lumens are lined by a highly mineralized cuff of peritubular dentine consisting primarily of apatite crystals (Ten Cate, 1998). Intertubular dentine occupies the regions between the tubules and consists of a collagen fibril mesh oriented essentially perpendicular to the tubules and bound by apatite crystallites. There is an increase in the number and size of the tubules as one moves from the periphery toward the pulp chamber (Pashley, 1989). There is also a gradual reduction in the tubule diameter with increasing age due to deposition of mineral within the lumens. A comparison of coronal dentine from two patients of different ages is presented in Fig. 12.1. Filling of the tubule lumens begins in the third decade of life. After an adequate degree of occlusion has taken place the tissue appears transparent and dentine that has undergone this change is regarded as ‘sclerotic’. Histological evaluations

(a)



(b)



12.1 Representative micrographs of young and old dentine. The tubules are oriented perpendicular to the plane of the page: *a* Young (20 year old female); *b* old (50 year old male).

have shown that dentine sclerosis begins in the root and progresses to the coronal dentine (Nalbandian *et al.*, 1960; Vasiliadis *et al.*, 1983a; Carrigan *et al.*, 1984; Micheletti Cremasco, 1998). Owing to the nature of deposited material, occlusion of the lumens results in an increase in the mineral content (Weber, 1974; Ketterl, 1983; Vasiliadis *et al.*, 1983b). As the mineral and collagen contents are regarded as the hard and tough components of the tissue (Marshall *et al.*, 1997), respectively, the structural changes in dentine with aging could cause an increase in brittleness and/or a reduction in the resistance to fracture. Nevertheless, the influence of aging on the

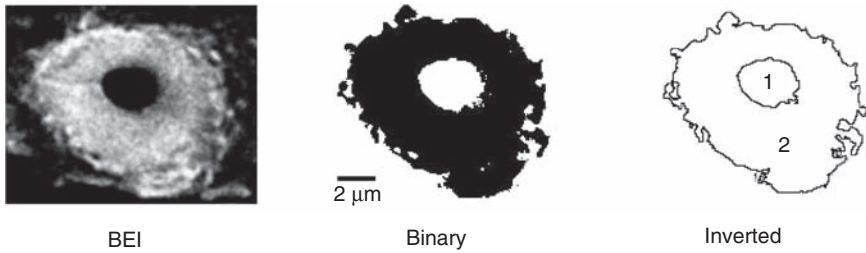
mechanical properties of dentine has received limited attention. This chapter aims to describe past and current research efforts addressing aging, structure and knowledge of their effects on the mechanical properties of human dentine.

12.2 Structure and chemistry

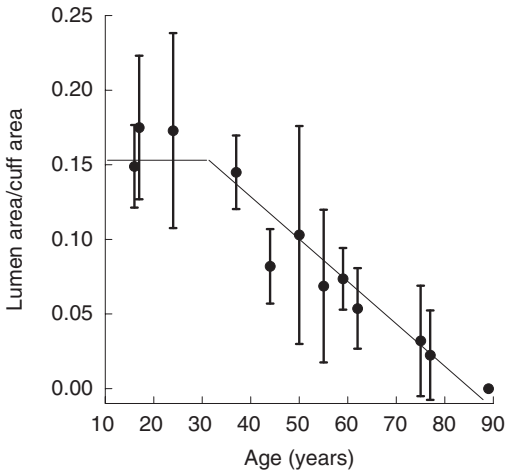
While it is now well recognized that dentine sclerosis begins in the apical root, there appears to be less knowledge of the progressive changes in structure that precede sclerosis, particularly in the coronal dentine. Transparency of the tissue in regions of sclerosis results from a decrease in the diffraction of light from about the lumens. Weber (1974) noted that not all tubules were occluded within transparent regions, which indicates that the initiation and progression of occlusion would be harder to recognize, and potentially least distinct in the coronal dentine. Yet, the progressive changes in structure and chemistry are particularly relevant to understanding the age-dependence in mechanical behavior. To address this need, the changes in lumen and peritubular cuff areas with age have been quantified using the scanning electron microscope (SEM) and a complementary image analysis. An example of a peritubular cuff examined in mid-coronal dentine using backscatter electron imaging (BSE) mode is shown in Fig. 12.2a. Due to the difference in their mineral content, BSE provides an effective means for differentiating between the lumen, peritubular cuff and the surrounding intertubular dentine. A quantitative description for the microstructure is then available through a summation of pixels corresponding to the lumen and distinct constituents. In Fig. 12.2a, a thresholding scheme has been used to reassign the continuous grayscale image to a binary image, which then enables a distinction of the image areas corresponding to the tubule lumen and the peritubular cuff. A quantification of the structural changes in mid-coronal dentine of fully erupted third molars using the ratio of lumen and peritubular cuff areas is shown in Fig. 12.2b. According to this distribution, there is a reduction in the lumen diameter beginning after the third decade of life and continuing with age monotonically to complete occlusion. Note that these results may not represent the nature of occlusion of anterior teeth or those that play a more active role in mastication.

In addition to the importance of microstructure to the mechanical behavior, changes in chemistry and mineralization with aging are potentially equally relevant. Few studies have been reported in this area, but there have been some exceptional evaluations of sclerotic dentine within the recent past (Balooch *et al.*, 2001; Kinney *et al.*, 2005; Porter *et al.*, 2005). In a comparison of normal and sclerotic dentine using x-ray computed microtomography it was found that there is a significant increase in the degree of mineralization within the transparent dentine (Kinney *et al.*, 2005)

(a)



(b)



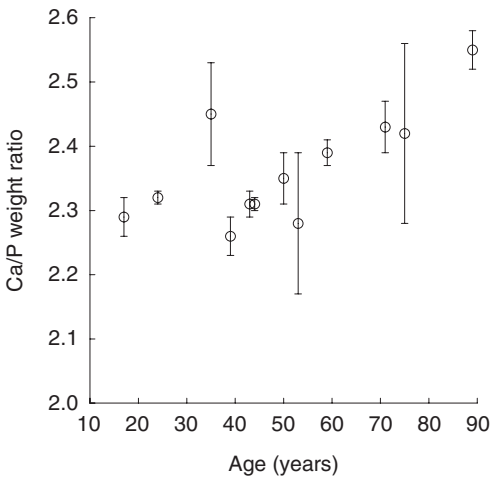
12.2 Quantitative measures for the changes in microstructure of dentine with age: *a* a representative using under BSE imaging, the binary image and inverted image for area measurements (example from 50 year old male); *b* Change in tubule dimensions with aging.

regardless of anatomical location. Furthermore, an evaluation of the inter-tubular dentine using small angle x-ray scatter (SAXS) suggested that sclerotic dentine (of patients aged 80 ± 14 years) exhibits a lower average crystallite size in comparison to normal (young: age = 24 ± 7 years) dentine. Further work by this group using transmission electron microscopy (TEM) distinguished that there is a reduction of the crystallite width in the inter-tubular dentine with sclerosis and that the mineral filling the tubule lumens consisted of much coarser grains with larger plate-like crystals. Micro x-ray analysis of the intratubular mineral showed that in addition to hydroxyapatite, some of the grains exhibited lattice plane spacing interpreted as CaO. Based on the combined results of these studies, the investigators postulated that occlusion of the lumens occurs by dissolution of intertubular crystals

and a re-precipitation of new mineral crystallites within the lumens (Porter *et al.*, 2005).

Similar to evaluations of structure, the progressive changes in chemistry with aging have not been examined in detail. One approach for examining the chemistry of hard tissues involves use of energy-dispersive x-ray analysis (EDX). Briefly, EDX is conducted within an SEM where the incident electron beam promotes emission of x-rays from the substrate. The x-ray energy corresponds to the material under examination and enables a measure of the near-surface chemistry (Garret-Reed and Bell, 2003). In evaluation of dentine, EDX enables determination of the calcium (Ca) and phosphorus (P) content, among other elements. A preliminary examination of coronal dentine was conducted using EDX and distinguished that there is an increase in the Ca/P weight ratio in dentine with aging (Fig. 12.3). Consistent with the onset and progression of occlusion (Fig. 12.2b), the process appears to begin after the third decade of life and continues with age thereafter. As evident from the individual measures of the Ca and P content, the rise in Ca/P ratio occurred primarily through an increase in the Ca. These results appear to agree with the identification of CaO in the intratubular regions of sclerotic dentine that was interpreted using electron diffraction measurements (Kinney *et al.*, 2005).

The aforementioned studies provide some additional understanding of the nature of structural and chemical changes with aging. According to the quantitative descriptions in Fig. 12.2 and 12.3, dentine appears to remain ‘young’ through the third decade of life and there are continuous changes



12.3 Increase in the Ca/P ratio of coronal dentine as a function of patient age. The chemical evaluation was conducted using EDX.

thereafter. It would be expected that these changes are reflected in the mechanical behavior of dentine; and this will be explored through the remainder of this chapter. Nevertheless, it is important to emphasize that the results presented in Fig. 12.3 represent a preliminary assessment of the changes that occur over a continuous age spectrum. There is considerably more work required to understand the chemistry associated with the onset and progression of occlusion, as well as the biological signals responsible for this process. Furthermore, the aforementioned studies have not addressed whether there are simultaneous and progressive changes in the collagen matrix with aging. These aspects of the aging process should be examined in more detail and coupled with future evaluations of chemistry.

12.3 Elastic behavior and strength

According to the higher mineral content, sclerotic dentine would be expected to exhibit differences in mechanical behavior when compared with normal (young) dentine. Balooch *et al.* (2001) were the first to examine properties of sclerotic dentine in detail and used an atomic force microscope (AFM) to achieve independent evaluations of the intertubular, peritubular and intratubular (filling the tubules) components. They found that there was no significant difference in either the hardness or elastic modulus between the intertubular and peritubular components of normal and sclerotic root dentine. Properties of the material filling the tubules within sclerotic dentine were between those reported for the intertubular and peritubular dentine. According to the consistency in chemistry of the peritubular and intratubular dentine (Kinney *et al.*, 2005), it would appear that the crystals formed within the lumens are less densely packed than in the peritubular wall. An evaluation of the elastic constants for root dentine using resonant ultrasound spectroscopy (RUS) also found no significant differences in either the Young's modulus or shear modulus between normal and sclerotic tissue. However, in a comparison of tissue from young (22 ± 3 years) and old (61 ± 6 years) patients, Senawongse *et al.* (2006) recently reported that there are regional differences in the hardness and elastic modulus of dentine with age. While properties of transparent and normal tissue were not significantly different, they identified that the old dentine just beneath the DEJ (within $5\mu\text{m}$ from the DEJ in the mantle dentine) exhibited larger hardness and elastic modulus. The increase in hardness was found to be concentrated in areas of enamel wear.

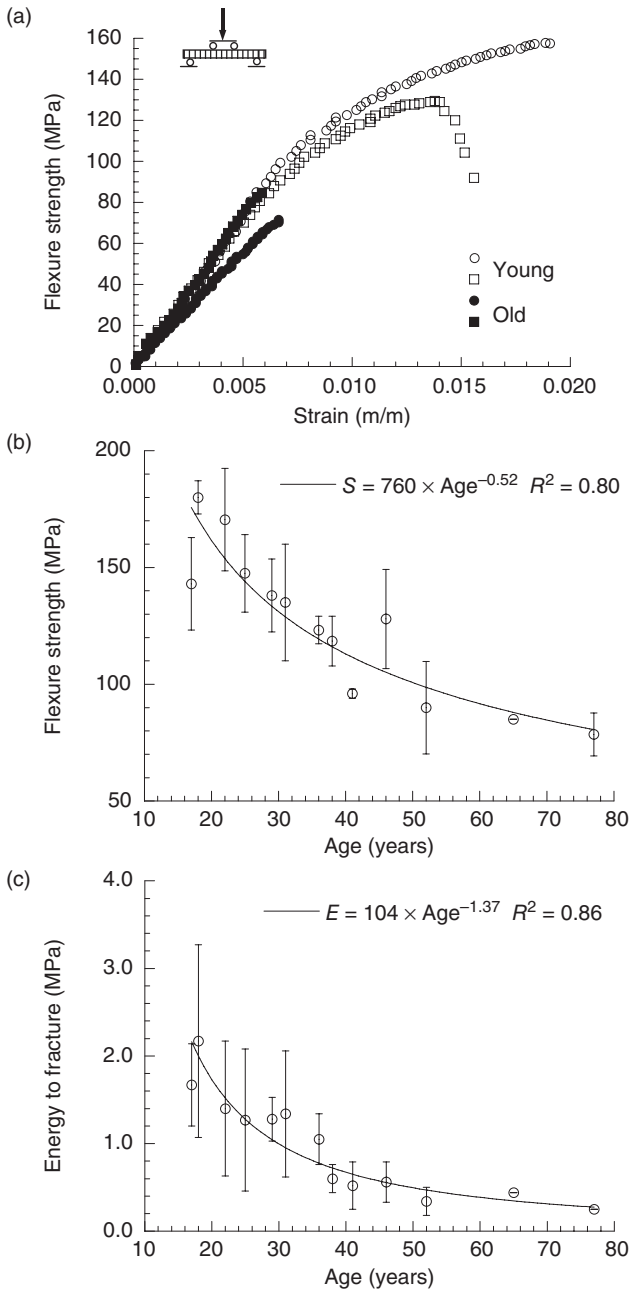
The author and his colleagues have been examining the importance of aging on the mechanical behavior of dentine under both static and fatigue loads (Arola and Reprogel, 2005, 2006). These investigations have been conducted using the coronal dentine of third molars obtained from patients ranging in age from 17 to 77 years old. Briefly, rectangular

beams are obtained using conventional diamond slicing equipment and then subjected to four-point flexure within a hydration bath of Hanks' balanced salt solution (HBSS) at 22°C. In the quasi-static evaluations, the load and load-line displacement are used with the beam geometry and flexural arrangement to generate stress-strain diagrams for the response.

Representative results from flexure tests are shown in Fig. 12.4a for specimens prepared with the dentine tubules aligned perpendicularly to the length and parallel to the plane of maximum normal stress. As evident in this figure, the dentine of younger patients exhibited linear elastic behavior, followed by a region of non-linear inelastic deformation to failure. In contrast, specimens obtained from older patients exhibited linear-elastic behavior only, and a lower strength and strain to failure in comparison with responses of the young tissue. The flexure strength distribution over the entire patient age range examined is shown in Fig. 12.4b. The energy to fracture can be obtained from the area under the flexural stress-strain curves and the distribution in this property with patient age is shown in Fig. 12.4c. There is a 50% reduction in strength and nearly a 90% reduction in the energy to fracture over the 60 year age span presented. Both the strength and energy to fracture undergo a decrease in magnitude throughout the period of aging, but the largest rate of reduction takes place shortly following eruption. Beyond age 50, the reduction in strength and energy to fracture were not significant. Interestingly, none of the beams examined were completely sclerotic. Therefore, in the coronal dentine there are significant changes in the mechanical behavior that take place before sclerosis. The property distributions in Fig. 12.4b and 12.4c suggest that the coronal dentine undergoes a transition in mechanical behavior and approaches a threshold near age ≥ 50 years. Earlier examinations of the structure and chemistry appeared to suggest that the tissue remained young for age ≤ 30 years. Using these definitions for characterizing the 'young' (age ≤ 30 years) and old (age ≥ 50 years) responses, the strength and energy to fracture of the old dentine are significantly lower ($p < 0.0001$) than those of the young dentine. However, there was no significant difference ($p > 0.05$) between the flexure modulus of the young (mean age, 24 ± 5 years) and old (mean age, 65 ± 13 years) tissue; the average flexure modulus of the dentine was 14.8 ± 2.6 GPa. These results are consistent with earlier evaluations in which there was no significant difference between the elastic modulus of normal and sclerotic dentine (Kinney *et al.*, 2005; Senawongse *et al.*, 2006).

12.4 Fatigue and fatigue crack growth

Fatigue failures can originate from existing inherent defects in a material that coalesce with cyclic loading and enable fracture through a reduction



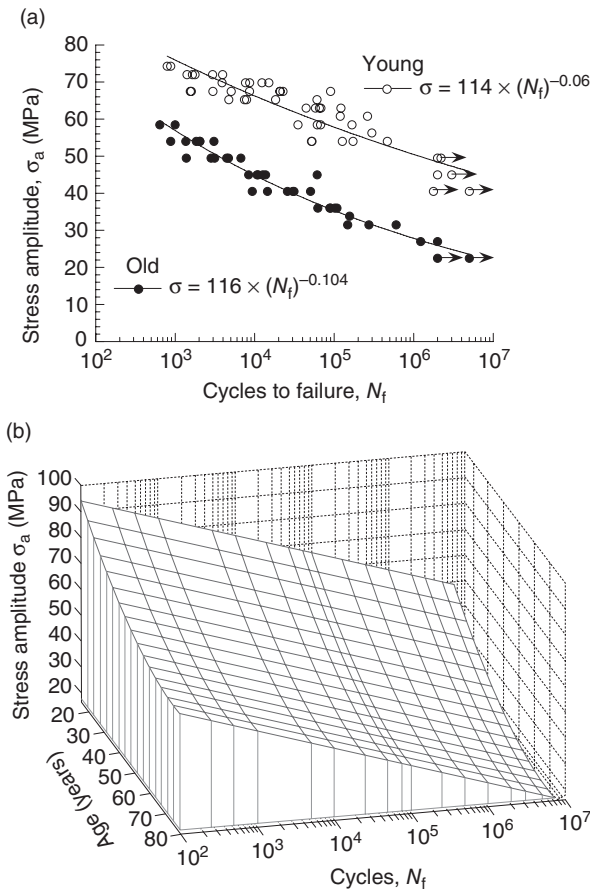
12.4 Mechanical properties of dentine in terms of the patient age: *a* typical flexural responses for dentine obtained from young (age = 17 years) and old (age = 77 years) patients; *b* flexure strength as a function of patient age; *c* energy to fracture.

in load-bearing capacity (i.e. stress–life fatigue). Alternatively, fatigue failures can originate from a well-defined flaw (or crack) that undergoes extension under cyclic loading until reaching a critical length (i.e. fatigue crack growth). In recognition of the nature of mastication, the fatigue of dentine, enamel and the materials used for replacing tooth tissues is a relevant concern. An understanding of the fatigue properties of dentine appears to be developing (Arola *et al.*, 2002, 2005; Arola and Rouland, 2003; Nalla *et al.*, 2003a, 2004; Arola and Reprogl, 2005, 2006; Kruzic *et al.*, 2005; Arola and Zheng, 2006; Bajaj *et al.*, 2006; Kruzic and Ritchie, 2006). However, the importance of aging has not been addressed in detail.

12.4.1 Stress–life fatigue

Tonami and Takahashi (1997) were the first to consider the importance of aging on properties of tooth tissues. They identified that the fatigue strength of ‘adult’ bovine dentine (46.9 MPa) was significantly less than that from the teeth of young animals (51.0 MPa). However, the difference in age between the two groups of animals was limited to only a few years. The author and his colleagues have examined the influence of aging on the fatigue behavior of human dentine. These studies were conducted using four-point flexural loading of beams prepared from the coronal dentine of third molars obtained from patients ranging from 17 to 80 years of age. Consistent with quasi-static experiments described earlier, the tubules were oriented perpendicular to the beam’s length (and parallel to the plane of maximum normal stress). Cyclic loads were applied under load-control actuation using a load ratio ($R = P_{\min}/P_{\max}$) of 0.1 and frequency of 5 Hz. A haversine load profile was used resulting in a maximum cyclic stress range ($\sigma_{\max} - \sigma_{\min}$) on the surface of the beams from 50 to 160 MPa; the stress distribution was estimated using simple beam theory (Popov, 1990). The cyclic maximum stress remained constant over the duration of testing and the minimum cyclic stress was always one-tenth of the maximum. All testing was performed within a hydration bath of HBSS at room temperature (22 °C). In these experiments, the maximum bend stress and the number of cycles to failure were recorded for individual beams and then used in constructing fatigue life (i.e. stress–life ($S-N$)) diagrams for dentine of specific age groups.

Fatigue life diagrams for young ($17 \leq \text{age} \leq 30$ years) and old (age ≥ 50 years) coronal dentine are shown in Fig. 12.5a. Power law models were developed to describe the mean response for each age group and are presented for reference. Regardless of the magnitude of cyclic stress, the old dentine exhibits a fatigue life that is significantly lower than that of young dentine. In evaluations of stress–life fatigue behavior, many materials exhibit an endurance strength, which represents a magnitude of cyclic stress



12.5 The influence of age on the fatigue strength of human dentine: *a* stress-life ($S-N$) diagrams for young (age <30 years) and old (age >50 years) dentine (data points with arrows indicate specimens that did not fail and cyclic loading was discontinued); *b* the master model for the age-dependent $S-N$ response.

below which failure does not occur, or takes a very long time. The responses for dentine do not exhibit well-defined endurance strengths, but an apparent value can be estimated using the power law models and a life (N_f) of 1×10^7 cycles. Using this approach, the young dentine exhibits an 'apparent' endurance strength of approximately 44 MPa. Using the same definition for old dentine, the apparent endurance strength is 23 MPa, nearly one-half that for young dentine. Results from the entire age spectrum were used in constructing a model for the fatigue strength using non-linear regression which is given by

$$\sigma_a = 135 - 1.3A + 0.008A^2 - 9\log(N_f) \quad [12.1]$$

where σ_a is the cyclic stress amplitude, A is age of the patient and N_f is the number of cycles to failure. The cumulative age-dependent S – N response for coronal dentine is presented in Fig. 12.5b. To the author's knowledge, these results represent the first continuous description for the age-dependent fatigue strength of a hard tissue.

Fatigue testing of the dentine specimens was conducted using a stress ratio that resulted in a non-zero mean stress. If the Goodman model (Goodman, 1899) is used to account for mean stress effects, the equivalent endurance strength for fully reversed loading (σ_e) of young and old dentine is 67 and 32 MPa, respectively. Using the flexure strength presented earlier in this chapter, the ratio of endurance strength to ultimate strength (σ_{ult}) in flexure for young and old dentine is approximately 0.5 and 0.38, respectively. These ratios are consistent with values that are often reported for many engineering structural materials ($0.3 \leq \sigma_e / \sigma_{ult} \leq 0.6$). Nevertheless, the smaller ratio for old dentine emphasizes the increased sensitivity to fatigue. It is expected that the reduction in fatigue strength with aging is attributed to an increase in the propensity for damage initiation from inherent defects and an increase in the rate of damage coalescence. In other words, dentine becomes less damage-tolerant with age. Overall, the observations suggest that fatigue failures will occur in old dentine at much smaller cyclic stresses than those that cause failure in young dentine, and they will occur within a shorter period of clinical function.

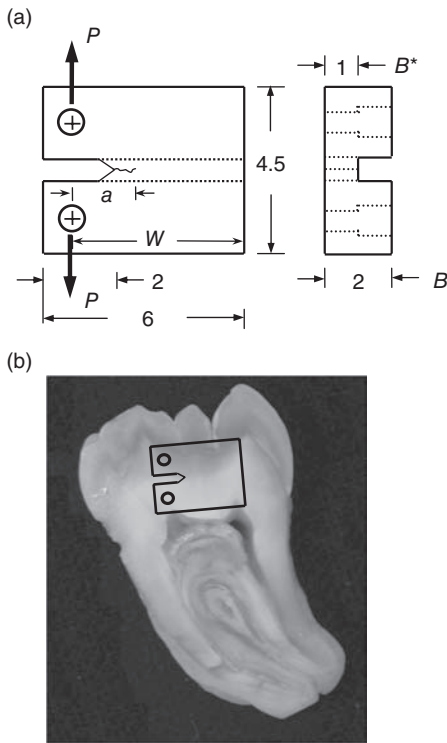
A recent study of sclerotic dentine examined the S – N fatigue behavior and reported that the largest difference in fatigue strength between normal and sclerotic dentine occurred at larger cyclic stress ranges (Kinney *et al.*, 2005). In fact, there was no difference between the high-cycle ($N \geq 10^5$) fatigue life responses. Using power law models presented for describing the fatigue strength distributions, the apparent endurance strength of the normal and sclerotic dentine at $N_f = 1 \times 10^7$ cycles are 27 and 33 MPa, respectively. These values are between those presented for young and old dentine determined in four-point flexure, and there is surprisingly almost no difference between the normal and sclerotic groups. That study was conducted on the root dentine of molars by flexure loading of cantilever beams at a loading frequency of 10 Hz. The cantilever configuration results in a non-constant normal stress along the beam's length and a superposition of normal and shear stresses. In addition, previous investigations have identified that the fatigue strength of dentine increases with an increase in loading frequency (Nalla *et al.*, 2003a). Most important to this comparison, the plane of fracture in Kinney *et al.* (2005) was described as being nominally perpendicular to the tubule direction, indicating that the tubules were normal to the plane of maximum normal stress. Fatigue of dentine is

dependent on tubule orientation and the largest fatigue strength is obtained when the tubules are parallel to the plane of maximum normal stress (Arola and Reprogel, 2006). Therefore, the contradicting influence of aging on the fatigue behavior in these two studies is expected to result from the difference in tubule orientation. One interpretation of the difference is that the effects of aging on the fatigue strength of dentine are orientation-dependent. Results from Arola and Reprogel (2006) suggest that the collagen fibrils suppress the growth of fatigue damage when aligned with the direction of cyclic normal stress, and their ability for toughening dentine diminishes with patient age. Additional work is needed to identify if the changes in fatigue properties with aging are orientation-dependent, and to distinguish the contribution of collagen in suppressing the initiation and propagation of damage in this tissue with cyclic loading. Perhaps equally important, it is not known whether there is an interaction between aging and gender that affects the aging process and diminution of fatigue strength. Both the potential for tooth fracture and characteristics of the fracture process could be dependent on the aforementioned concerns. Further work is necessary to address adequately these issues.

12.4.2 Fatigue crack growth

Cyclic loading can also promote existing flaws and/or cracks to undergo extension through a process regarded as fatigue crack growth. This process can play a pivotal role in restored tooth failures as it represents a very viable scenario for tooth fracture. If flaws are introduced within the hard tissue foundation during restorative processes, they may undergo cyclic extension under the forces of mastication, thereby facilitating tooth fracture (Arola *et al.*, 1999). As such, dentine's resistance to fatigue crack growth is an important aspect of material behavior.

The author and his colleagues have ongoing studies aimed at understanding the effects of aging on fatigue crack growth in human dentine. These studies utilize compact tension (CT) specimens prepared from the coronal dentine of second and third molars that were obtained from patients from 17 to nearly 90 years of age. The specimens are sectioned from the molars under hydrated conditions using a commercial slicer/grinder with diamond-impregnated slicing wheels. A schematic diagram of the CT specimen geometry is shown in Fig. 12.6a. The specimen configuration enables the initiation of a crack from a prepared notch and crack extension under cyclic opening mode (Mode I) loads. Note that the specimen has a channel introduced on one side that serves to reduce the specimen's apparent thickness (from B to B^*) along the projected path of crack growth. Preliminary experiments showed that a channel was required to control the direction of extension for specific tubule orientations (Arola *et al.*, 2002). Also,



12.6 Development and fatigue testing of the dentin CT specimens (dimensions in millimeters; *a* details of the specimen geometry; *b* a CT specimen prepared from the coronal dentine of a third molar subjected to cyclic loading).

specimens prepared without the channel commonly fractured at the loading holes during cyclic loading. The reduction in cross-section thickness about the channel enabled lowering of the cyclic load magnitude. Additional details regarding the methods of specimen preparation have been presented elsewhere (Bajaj *et al.*, 2006).

Fatigue crack growth testing of the dentine CT specimens is achieved using commercial universal testing equipment (Bose, Electroforce Model 3100 and Model 3200). The initiation of a crack from the notch root is achieved by grinding in a sharp notch with a razor blade and diamond paste, followed by a preliminary period of cyclic loading. The initiation period utilizes a cyclic load with load ratio ($R = P_{\min}/P_{\max}$) of 0.5 and frequency of 5 Hz. Following crack initiation, cyclic loading is applied using load control actuation with $R = 0.1$ and frequency of 5 Hz. Crack initiation is conducted at higher load ratios to accelerate the rate of initiation (Arola *et al.*, 2005).

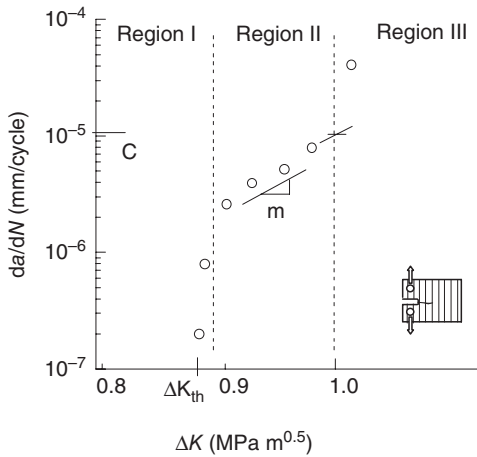
In both initiation and growth phases, the peak load of the waveform ($P_{\max}$) is generally $8 \leq P_{\max} \leq 12\text{N}$ and is chosen according to the position of the pre-notch and crack initiation behavior. The loading process is conducted in intervals (e.g. 50 kcycles), after which the crack length is measured using an optical microscope ($\times 100$) with scaled reticule. Clarity of the crack tip is achieved by staining the front face of the specimen (without channel) using an indelible marker and illuminating it from the back of the specimen (with channel) using a focused beam of white light. Each interval of cyclic loading (ΔN) provides a new measurement of crack extension (Δa), which results in acquisition of data pairs (Δa , ΔN) over the total crack growth history until complete specimen fracture. The number of cycles between measurements typically ranges between 10000 and 50000 cycles. Including the periods of crack initiation and extension, a single experiment generally extends over 3–6 days and the time between extraction of the tooth and completion of the experiments is restricted to less than 1 month. All testing is conducted within a hydration bath of HBSS at room temperature (22°C). According to a study by Habelitz *et al.* (2002), the changes in mechanical properties of dentine maintained in HBSS over this period are negligible.

Using the incremental crack length measurements obtained after each interval of cyclic loading, the fatigue crack growth rate (da/dN) is plotted in terms of the stress intensity range (ΔK) on a log–log scale to interpret characteristics of the response. Due to the unique geometry of the dentine CT specimens, a dedicated model for the ΔK distribution was developed according to a numerical analysis of the energy release rate with crack extension (Bajaj *et al.*, 2006). For cyclic opening mode (Mode I) loading, the stress intensity is described by

$$K_I = \frac{P}{B^* \sqrt{W}} \left(\frac{B^* + 1}{B + 1} \right)^{0.5} (0.131 + 0.320\alpha + 0.211\alpha^2) \quad [12.2]$$

where: P is the magnitude of opening mode loading; B^* , B and W are geometric parameters as described in Fig. 12.6a; and α is a numerical value equal to the ratio of average crack length over the growth increment $[(a_i + a_{i-1})/2]$ to W . The ΔK for cyclic loading is computed using Eqn. [12.2] by replacing the load with the load range (ΔP), which is estimated from the difference in maximum and minimum cyclic loads ($P_{\max} - P_{\min}$).

A typical fatigue crack growth response for a dentine CT specimen is presented in Fig. 12.7. The entire response from crack initiation to fracture has been divided into three distinct regions. Region I is regarded as the near-threshold region and is associated with the initiation of cyclic crack extension. The second region (Region II) represents the ‘steady-state’ region of cyclic crack growth and is often regarded as the ‘Paris’ region. Region III describes the unstable region of fatigue crack growth as the crack progresses towards a critical length that enables fracture. Region II



12.7 A typical fatigue crack growth response for a dentine CT specimen ($\theta = 90^\circ$). In evaluating fatigue crack growth responses using the Paris law, m is the slope of the Region II response and quantifies the sensitivity of the material to the crack length (and resulting stress intensity). The crack growth coefficient (C) is the y -intercept of the Region II response (at $\Delta K = 1$) and quantifies the effective growth rate of the material. Lastly, the stress intensity threshold (ΔK_{th}) is the x -intercept of the Region I response extrapolated to the ordinate and quantifies the minimum stress intensity required for cyclic extension.

is often distinguished from the other two as the portion of cyclic extension with minimum slope. Due to the comparatively low growth rate within this region, it generally constitutes the majority of the fatigue life (Suresh, 1998). Traditionally, it has been the region of most interest in evaluating a material's resistance to fatigue crack growth. The Region II behavior can be conveniently quantified using the Paris law (Paris and Erdogan, 1963) according to

$$\frac{da}{dN} = C(\Delta K)^m \quad [12.3]$$

where ΔK is the stress intensity range, and da and dN represent the incremental crack extension (Δa) and number of load cycles (ΔN), respectively. The quantities m and C are defined as the fatigue crack growth exponent and coefficient, respectively, and are considered material constants. When evaluated on a log-log scale the quantities m and C are simply the slope and y -intercept deduced from the linear trend line. These two measures quantify the sensitivity of the material to fatigue crack growth extension and the effective growth rate, respectively. Note that there are other analytical expressions available for modeling fatigue crack growth, but

these are often reserved to account for the influence of additional factors (e.g. stress ratio, frequency, etc.) on the growth response.

In evaluations of fatigue crack growth in young coronal dentine ($17 \leq \text{age} \leq 35$ years), specimens have been prepared with tubule orientations parallel (0°), oblique (45°) and perpendicular (90°) to the direction of crack extension (Arola *et al.*, 2007). Note that the age range has been expanded slightly with respect to earlier definitions due to difficulties in obtaining molars with adequate size for the 45° orientation. For the 0° orientation, the tubules were aligned with the fracture surface and perpendicular to the direction of crack extension. The Region II growth responses for specimens with 0° and 90° orientations are shown in Fig. 12.8a; results for the 45° specimens have been excluded for clarity. The Paris law parameters presented in this figure were obtained by pooling the fatigue crack growth data of all specimens with the specific orientations. Regardless of the tubule orientation, steady-state fatigue crack growth within the young tissue occurred over $0.65 \leq \Delta K \leq 1.2 \text{ MPa m}^{0.5}$. The average cyclic growth rate is approximately $1.2 \times 10^{-5} \text{ mm/cycle}$ and occurred at a ΔK of approximately $0.85 \text{ MPa m}^{0.5}$. In examining the Paris law exponents estimated from the pooled data, values for the 0° , 45° and 90° tubule orientations are 7.9, 5.2 and 12.5, respectively. Fatigue crack growth parameters calculated from the average of results from individual specimens are listed in Table 12.1. The larger slope (m) for the 90° orientation indicates that dentine is most sensitive to the stress intensity (and presence of a flaw) when the crack is oriented perpendicular to the tubules. Additional details concerning anisotropy in the fatigue crack growth responses of dentine have been presented elsewhere (Arola *et al.*, 2007).

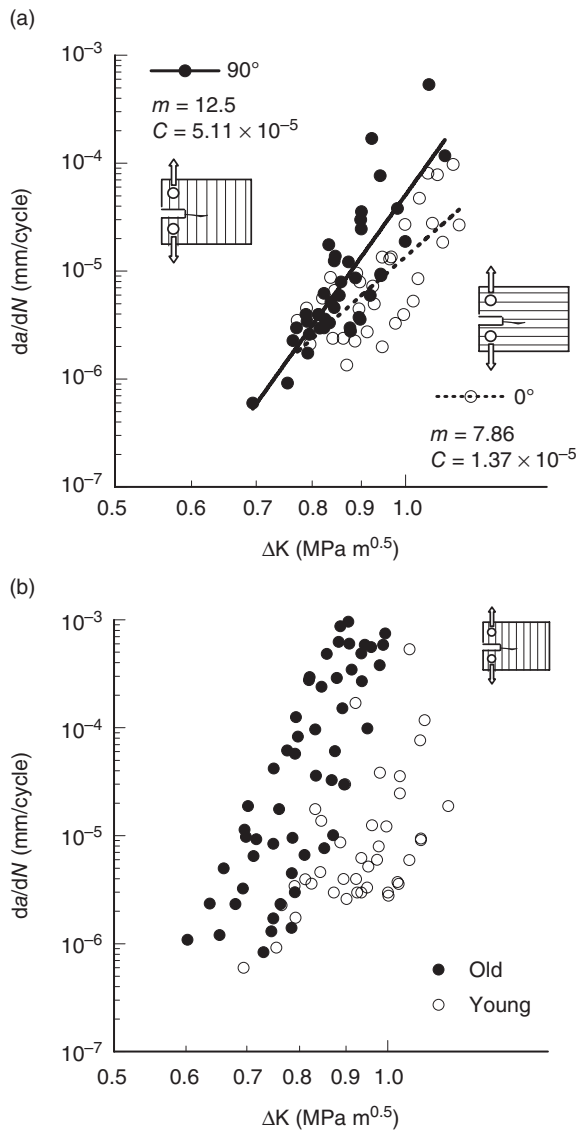
Studies concerning the influence of aging have concentrated on the tubule orientation with highest apparent sensitivity to fatigue crack growth (90°).

Table 12.1 Average Paris law parameters for fatigue crack growth. Results for young dentine include three unique tubule orientations ($\theta = 0^\circ, 45^\circ, 90^\circ$). Groups with the same letter are not significantly different.

Group (<i>N</i>)	Age (years)	<i>m</i>	<i>p</i> **	<i>C</i> (*)	<i>p</i> **
Young					
$\theta = 0^\circ$ (8)	25	12.5	ab	1.58×10^{-5}	a
$\theta = 45^\circ$ (8)	26	11.1	b	8.13×10^{-5}	b
$\theta = 90^\circ$ (9)	25	13.3	a	1.74×10^{-5}	ab
Old					
$\theta = 90^\circ$ (8)	55	21.6	c	2.90×10^{-2}	ab

* Units are $(\text{mm/cycle}) \times (\text{MPa m}^{0.5})^{-m}$.

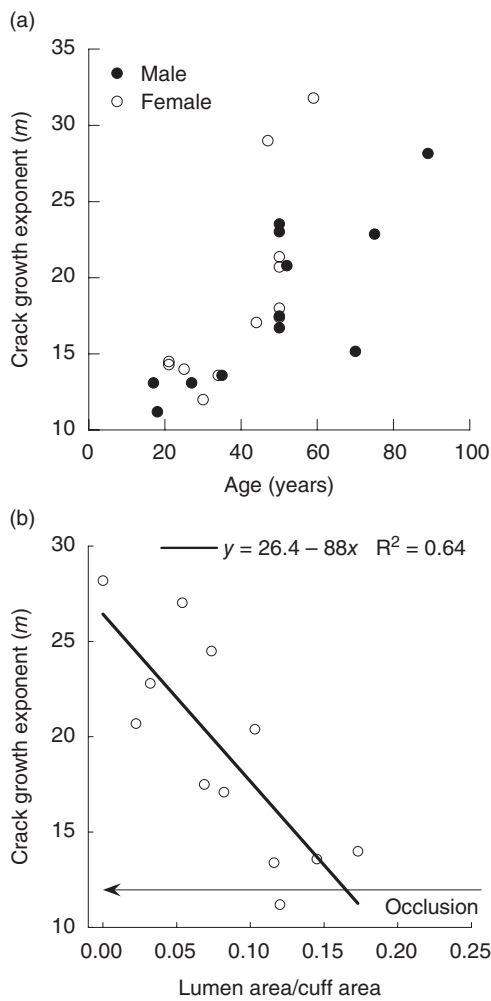
** a-b, $p < 0.05$; a-c and b-c, $p < 0.001$.



12.8 Fatigue crack growth in human coronal dentine: *a* a comparison of growth responses in CT specimens with tubules oriented parallel (0°) and perpendicular (90°) to the direction of crack extension; *b* a comparison of the growth responses within young and old dentine. All of the data are for growth perpendicular to the dentine tubules (90° orientation).

A comparison of the Region II crack growth responses for young and old (age ≥ 50 years) dentine are shown in Fig. 12.8b. As evident from the steady-state growth responses in this figure, the old dentine has a lower resistance to fatigue crack growth. The average fatigue crack growth exponent for the old dentine ($m = 21.6 \pm 5.2$) is significantly greater ($p < 0.001$) than that of the young hydrated dentine, regardless of the tubule orientation. Similar to the increase in m , the crack growth coefficient (C) for the old hydrated dentine is greater than that for the young hydrated dentine, and is approaching significance ($p = 0.07$). Although there are clear differences in the Paris law parameters, the importance of age is most evident in the average rate of fatigue crack growth. For a stress intensity range of $0.85 \text{ MPa m}^{0.5}$, the average rate of fatigue crack growth in the young hydrated dentine is $2 \times 10^{-6} \text{ mm/cycle}$. At the same ΔK , the average growth rate in the old dentine is $9 \times 10^{-4} \text{ mm/cycle}$, which is more than 100 times that in young dentine. Thus, cracks introduced within dentine during routine restorative procedures, or which develop through coalescence of intrinsic defects, are far more likely to cause tooth fracture in senior patients, and within a shorter period of oral function.

Regardless of age, the Paris law exponent for fatigue crack growth in human dentine is greater than that reported for bone (2.8–9.5) (Wright and Hayes, 1976; Nalla *et al.*, 2005a) and bovine dentine (2.7–4.6) (Arola and Rouland, 2003; Arola *et al.*, 2005), and slightly lower than that for elephant tusk dentine (12–32) (Kruzic *et al.*, 2005). The difference in m values between these hard tissues appears to signify the influence of structure on the mechanisms of fatigue crack growth. In examinations of engineering materials, ductile metals, which are considered resistant to cyclic crack growth, exhibit exponent (m) values near to 2. Brittle materials exhibit comparatively large fatigue crack growth exponents (typically $m \geq 4$) (Suresh, 1998) and are more sensitive to flaws. In general, m provides an indirect measure of the ‘brittleness’ of the material. The fatigue crack growth exponents for all specimens with tubule orientation of 90° are presented in terms of patient age in Fig. 12.9a. As expected, there is an increase in m with age, highlighting the increase in sensitivity to fatigue crack growth. Interestingly, the preliminary results presented in Fig. 12.9a suggest that gender may also be important to the nature of property changes with aging as well. This comment is speculative and fueled mostly by the well-recognized hormonal changes occurring in women with age. Additional work is necessary to determine whether the aging process progresses differently in the dentine of male and female patients. As the organic and inorganic components represent the tough and brittle components of the tissue, respectively, the increase in mineral content resulting from occlusion of the lumens would be expected to materialize in the apparent fatigue crack growth resistance. The change in crack growth exponent with occlusion is plotted in terms of



12.9 The influence of age and structure on the Paris law exponent for fatigue crack growth in human dentine: *a* the increase in crack growth exponent with age of the patient for dentine with $\theta = 90^\circ$; *b* the increase in fatigue crack growth sensitivity with occlusion of the tubules. Note that the degree of occlusion increases with a decrease in the ratio of lumen and cuff area.

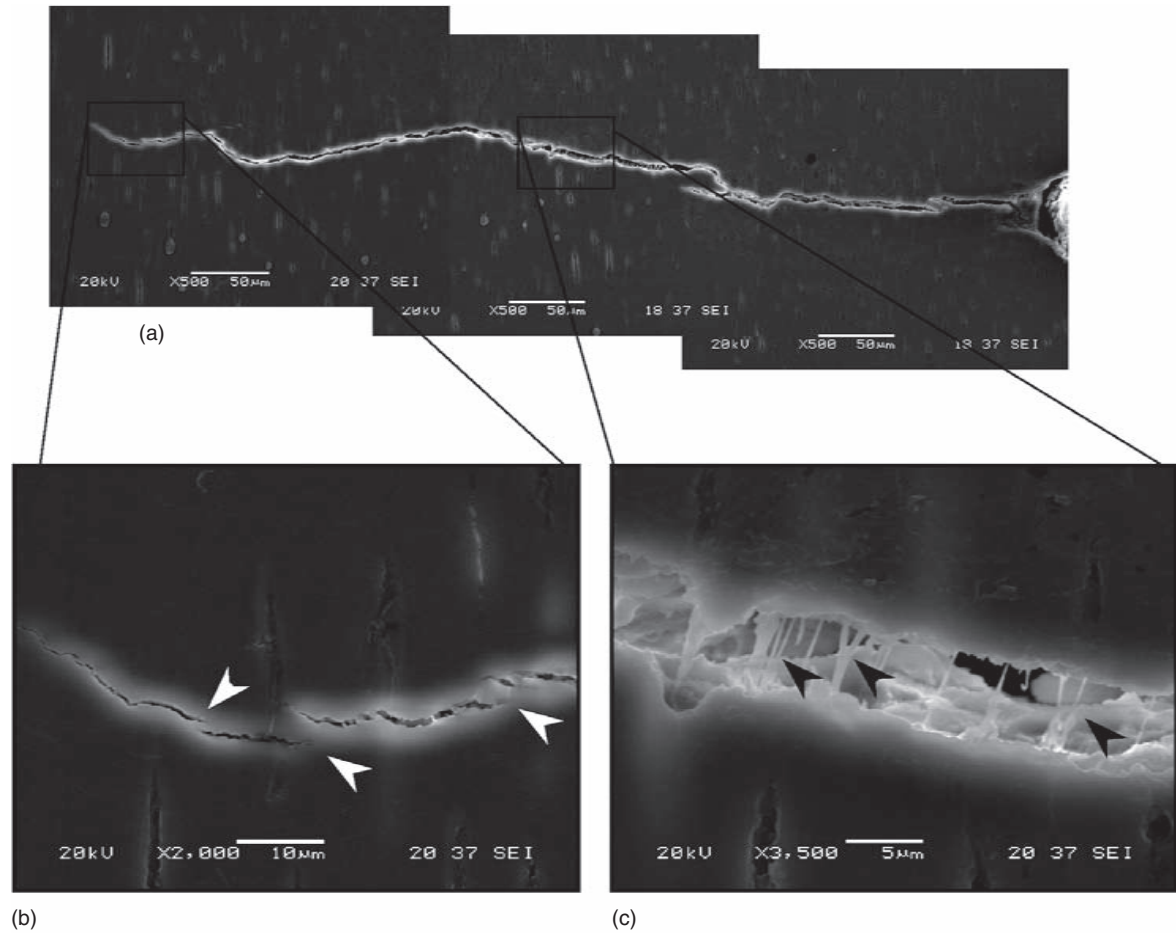
the ratio of lumen and cuff areas for selected specimens in Fig. 12.9b. Indeed, m increases with the quantitative description for the degree of occlusion and there is a high degree of correlation ($R^2 = 0.64$) between the structure and the fatigue crack growth response.

The stress intensity threshold (ΔK_{th}) represents a critical stress intensity range below which an existing crack will remain essentially dormant and/or

fatigue crack growth will not occur. It is often regarded as a measure of resistance to the onset of fatigue crack extension. A distinction of the ΔK_{th} in the fatigue crack growth response of young dentine was presented in Fig. 12.7. A ΔK_{th} was not readily apparent in the growth responses of all specimens, and was particularly difficult to identify in the experiments conducted with old dentine. However, a first-order estimate for ΔK_{th} can be obtained by extrapolating the Region II growth response to an appreciably small growth rate (e.g. 1×10^{-7} mm/cycle). Utilizing this approach for the responses in Fig. 12.8 suggests that the ΔK_{th} for young hydrated dentine is near to $0.65 \text{ MPa m}^{0.5}$. Results presented in Fig. 12.8b for the old dentine show that the first-order approximation for ΔK_{th} is closer to $0.5 \text{ MPa m}^{0.5}$. While these values for ΔK_{th} are comparatively small when compared with those for more common engineering structural materials (Ritchie, 1999), the lower value for old dentine indicates that cracks will undergo extension under smaller driving forces and that fatigue crack growth will occur from smaller flaws in the dentine of senior patients.

A material's apparent resistance to fatigue crack growth is dependent on the energy required for the development of new surface area (i.e. fracture) and the contributing mechanisms to crack extension. For most common structural materials, these mechanisms are well known, and can generally be classified according to whether the material exhibits predominately ductile or brittle behavior. As expected from the hierarchical microstructure and combination of both organic and inorganic components, the mechanisms of fatigue crack growth in dentine are far more complex. An interesting mechanistic description has been offered by Kruzic *et al.* (2005) based on experimental observations and suggests that crack propagation is comprised of a true cyclic fatigue crack growth mechanism that includes alternating blunting and resharpening of the crack tip. Crack extension occurs through microcracking ahead of the crack tip, which initiates at defects or the tubule lumens as a result of the effective stress concentration and high mineral content of the peritubular cuff. Extrinsic toughening (behind the crack) occurs through crack-bridging by a combination of collagen fibrils and ligaments of unbroken tissue that develop in the crack's wake. The combination of bridging elements facilitates crack growth retardation through a reduction in driving force at the crack tip. These specific mechanisms of toughening were also active and evident from an examination of fatigue cracks in the young dentine specimens, as shown in Fig. 12.10.

Crack-tip blunting is also an important aspect of the mechanisms of fatigue crack growth in dentine. Blunting is associated with near-tip non-linear deformation, which can arise from the near-field microcracking, and a component of time-dependent deformation that is potentially attributed to the viscoelastic/viscoplastic response of the collagen network. A quantitative assessment of the propagation mechanisms in dentine suggests that



12.10 Mechanisms of toughening evident from fatigue crack growth in the coronal dentin obtained from a 19 year old male patient: *a* fatigue crack originating from the notch (x500); *b* ligaments of dentine bridging the crack near the apparent tip (white arrows); *c* collagen fibrils (black arrows) spanning the crack behind the crack tip.

blunting and closure forces caused by bridging of unbroken ligaments appear to be the most significant contributors to the crack growth resistance (Nalla *et al.*, 2003b). Recent studies in the author's laboratory suggest that the time-dependent component of deformation is potentially also attributed to a hydraulic phenomenon (Arola *et al.*, 2005). Through cyclic loading, the non-linear component of deformation appears to be exhausted due to the redistribution of moisture. After sufficient fatigue, the local near-tip region becomes 'embrittled' and enables an increment of crack growth, which extends to the hydrated envelope. An examination of fatigue striations on the fracture surfaces of human dentine that form as a result of cyclic crack extension provides further evidence of this possibility (Bajaj *et al.*, 2007).

The increase in sensitivity to fatigue crack growth (m) with age and corresponding increase in the rate of cyclic extension signifies that there is a change in the mechanisms. One obvious contribution would be the potential reduction in microcracking ahead of the crack tip due to occlusion of the lumens. Sclerotic tissue would be most susceptible, as discussed by Kinney *et al.* (2005). A reduction in the number of microcracks would also result in a decrease in the formation of uncracked ligaments of dentine bridging the crack. In general, fewer ligaments have been observed during cyclic crack extension in the old dentine specimens. Due to the lower ultimate strength (Fig. 12.4b) and fatigue strength (Fig. 12.5) unbroken ligaments of old dentine would not be capable of providing the same degree of bridging forces as those that develop in young dentine. Lastly, dentine appears to lose its potential for non-linear inelastic deformation with age, as evident from the reduction in strain to fracture. While not identified explicitly, it is expected that there is a reduction in the capacity for viscoelastic/viscoplastic deformation in dentine with age, and this is expected to be due, at least in part, to degradation of the organic components. Further studies concerning the physical and chemical changes of the collagen matrix with aging are needed.

While there are obvious changes in structure that contribute to the reduction in fatigue crack growth resistance of dentine with age, the relative importance of individual changes that are taking place in concert have yet to be distinguished. Specifically, the increase in 'brittleness' with age can be conveniently attributed to the rise in mineral content associated with occlusion of the lumens and the consequent transformations in the mechanisms of fatigue crack growth. However, the role of the collagen matrix, and potential changes in this system with age are not understood. The development of methods for successfully repairing cracks and 'healing' damaged tooth structure requires a greater depth of understanding of the roles of both the organic and inorganic components in providing resistance to crack extension. This information is also of critical importance in conceiving

possible strategies for toughening of hard tissues. There is certainly more work ahead.

12.5 Fracture

Chapter 10 described the clinical importance of the fracture toughness of materials and testing methods. It also presented a review of studies examining the mechanics of fracture in dentine. Existing published work shows that dentine exhibits anisotropic fracture behavior (Iwamoto and Ruse, 2003; Nalla *et al.*, 2003b; Wang, 2005), it undergoes an increase in toughness with crack extension (i.e. *R*-curve behavior) (Kruzic *et al.*, 2003), and dehydration influences the apparent toughness (Kahler *et al.*, 2003; Nalla *et al.*, 2005b, 2006). Aging presents a new and growing concern.

Research on the influence of aging on fracture of human dentine is presently underway and complements the examinations of fatigue crack growth. The experiments are presently conducted using CT specimens prepared from the coronal dentine of third molars ($17 \leq \text{age} \leq 80$ years) with tubules oriented perpendicular to the plane of fracture and direction of crack growth. The specimen geometry was presented in Fig. 12.6a. Before testing, the specimens are subjected to cyclic loading using methods and equipment outlined in the previous section to initiate a well-defined crack from the prepared notch. The specimens are also subjected to a surface preparation that involves the deposition of a very thin layer (approximately $20\mu\text{m}$) of diluted correction fluid with addition of toner powder; this enables application of imaging techniques for identifying the crack tip and examining the mechanics of fracture. Additional details of the specimen preparation have been described elsewhere (Zhang *et al.*, 2007).

Quasi-static loading of the CT specimens is achieved using a specially designed miniature universal loading frame that is complimented with a stereomicroscope (SMZ-800 Steromicroscope; Nikon, Tokyo, Japan), charge-coupled device (CCD) camera (CV-A1 CCD camera; JAI America Inc., Laguna Hills, CA) and supporting imaging equipment. The loading frame is fully automated, enables load or displacement control actuation and has a load range of 100 N with precision of 0.05%. In addition, the frame utilizes a central lead screw with both left- and right-hand lead which results in simultaneous actuation of both grips in opposite directions and minimizes changes in the field of view that are typical with single-lead systems. Crack growth is monitored visually with the stereomicroscope and quantitatively through a correlation of digital images acquired throughout the period of stable extension. The optical system allows up to $\times 180$ magnification using the aforementioned microscope and camera. A single computer is used to control the load frame and sample the load and displacement

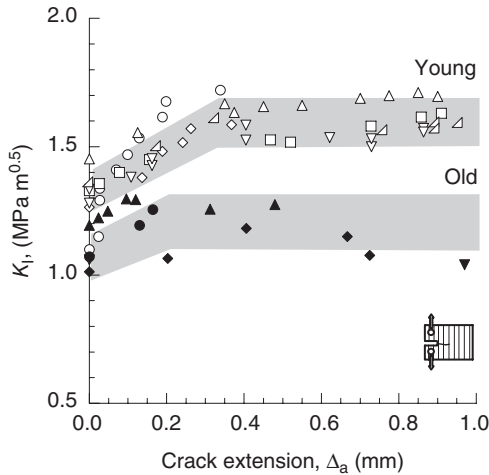
data, as well as to acquire and synchronize the digital images with the load/displacement response. Hydration of the specimens is maintained through use of a sponge that cradles the specimen and is saturated with HBSS throughout testing using an eyedropper.

An individual experiment consists of subjecting the CT specimens to Mode I loads, and acquisition of digital images before and during crack growth. Loading is applied under displacement control actuation in increments until the crack begins to extend; the displacement increments are chosen to result in 0.5 N reaction loads and smaller. After this period, the crack is extended incrementally through application of modest increases in load under displacement control. Digital images are acquired throughout the loading and growth process. Crack length measurements are obtained by post-processing the digital images using digital image correlation (DIC) (Zhang and Arola, 2004). Briefly, the full-field displacement distribution is calculated from the grayscale distribution of the speckles and the crack tip is identified from the position corresponding to zero opening mode displacement. Then, the stress intensity is calculated using the load and crack length measurements according to Eqn [12.2]. The apparent stress intensity (K_I) is quantified over the growth history to describe the resistance to crack growth as a function of crack extension (Δa).

Crack growth resistance curves (*R*-curves) obtained from experiments with CT specimens of young (age ≤ 30 years) and old (age ≥ 50 years) coronal dentine are presented in Fig. 12.11. Stable crack extension was possible in most specimens for between 1 and 2 mm of crack growth, with the largest degree of extension achieved in the young tissue. Overall, the responses in Fig. 12.11 show that there is a reduction in crack growth resistance with age. To aid in characterization, the initiation toughness (K_{I0}) has been defined at the inception of crack extension, a growth toughness (K_{Ig}) is used to quantify the increase in toughness with crack extension, and a critical stress intensity (i.e. fracture toughness, K_{Ic}) is defined at either the plateau (if stable extension is achieved) or maximum toughness (in the case of unstable growth). The K_{I0} values for the young ($1.4 \pm 0.1 \text{ MPa m}^{0.5}$) and old ($1.1 \pm 0.1 \text{ MPa m}^{0.5}$) groups are significantly different ($p < 0.01$).

Interestingly, the growth toughness is near $1 \text{ MPa m}^{0.5} \text{ mm}^{-1}$ for all of the specimens, regardless of age, except for the oldest sample (age = 83 years), which did not undergo toughening ($K_{Ig} = 0$). The average values of K_{Ic} for young and old dentine are 1.20 ± 0.1 and $1.65 \pm 0.1 \text{ MPa m}^{0.5}$, respectively, and these are significantly different ($p < 0.001$). According to these preliminary results, there is a decrease in the fracture toughness of human dentine with age, and the reduction over the 60 year period of aging examined exceeded 25%.

The *R*-curves presented in Fig. 12.11 represent the first descriptions for the age-dependent crack growth resistance behavior of human dentine. As



12.11 Crack growth resistance curves for human dentine of young (age ≤ 30 years) and old (age ≥ 50 years) patients. The responses are characterized in terms of an initiation toughness (K_c), a growth toughness (K_g) and an apparent critical stress intensity (K_c) defined at instability.

such, the data available for direct comparison are rather limited. The fracture toughness estimated for young dentine ($K_c = 1.65 \text{ MPa m}^{0.5}$) is in agreement with results of previous investigations on human dentine. In studies with the tubules oriented perpendicularly to the plane of crack growth (90°), Imbeni *et al.*, (2003) reported $K_c = 1.79 \pm 0.05 \text{ MPa m}^{0.5}$ and Iwamoto and Ruse (2003) found $K_c = 1.13 \pm 0.36 \text{ MPa m}^{0.5}$. Patient age was not specified in either of these studies. Perhaps most relevant, a recent study of transparent dentine (age ≥ 65 years) reported a mean K_c of $1.46 \pm 0.11 \text{ MPa m}^{0.5}$ for the 90° tubule orientation (Kinney *et al.*, 2005) which is within the range presented in Fig. 12.11, but higher than that for the old dentine. Results from the preliminary studies confirm that there is a reduction in the fracture toughness of human dentine with patient age. One of the most important findings is that the reduction in toughness is not limited to tissue that has undergone sclerosis (i.e. complete occlusion of the dentine tubules). However, it is not yet possible to identify the age at which the changes begin, and if they occur uniformly over an individual's lifetime. Aging may also initiate differently within teeth that play a greater role in mastication due to both mechanical and hydraulic processes. These concerns remain to be addressed.

Despite the large range in patient age, nearly all the dentine samples exhibited a growth toughness near $1 \text{ MPa m}^{0.5} \text{ mm}^{-1}$. The rise in toughness with crack extension in dentine has been attributed to ligaments of unbroken

tissue and collagen fibrils that reduce the apparent stress intensity through development of posterior bridging stresses (Kruzic *et al.*, 2003; Nalla *et al.*, 2003b). Ligaments of dentine were observed during the experiments identical to the observations of fatigue crack growth as shown in Fig. 12.10. The extent of toughening would be expected to decrease with patient age due to a reduction in ligament strength. Indeed, the number of unbroken ligaments was far fewer in the old dentine specimens. Furthermore, the growth responses in Fig. 12.11 show that toughening occurred over a much smaller extent of crack extension (0.2 mm) in comparison with the responses for young dentine (0.4 mm). Although the reduction in process zone is at least partly due to a decrease in ligament strength, there are probably other important contributions that remain to be identified. Additional experiments are required to make more substantial statements regarding the specific differences in toughening mechanisms between young and old dentine. Future investigations on aging and fracture that are coupled with an examination of the microstructure and chemistry of dentine are necessary and will contribute to the development of a fundamental understanding.

12.6 Summary

With the progressive increase in partially and fully dentate seniors, the influence of aging on properties of the human tooth has become of substantial importance in the pursuit of lifelong oral health. A presentation of current and ongoing investigations addressing aging and its importance to the mechanical behavior of human dentine has been presented in this chapter. Preliminary studies show that there are both structural and chemical changes in dentine that initiate after the third decade of life. Results of recent experimental evaluations show that these changes are detrimental to the mechanical behavior under both static and cyclic loading conditions. In particular, dentine undergoes a decrease in strength, as well as a reduction in the resistance to crack extension under both quasi-static and cyclic loading. Nearly all measures of mechanical behavior suggest that aging promotes an embrittlement of dentine. While the evolution in properties appears to stem from the onset and progression of minerals filling the lumens, contributions from the collagen matrix remain unknown. Further knowledge is needed on the relative roles of the organic and inorganic components in the aging process, and the nature of biological signals responsible for the initiation and progression of the structural changes. Future studies should also address whether the nature of aging is gender-specific. This knowledge will help to identify patient characteristics and/or treatment conditions that are most detrimental to the fatigue and fracture resistance. Opportunities for toughening dentine, and/or therapies capable of retarding

the aging process will require further studies that are tightly coupled with evaluations of the microstructure and chemistry.

12.7 Acknowledgements

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Finite element analysis of stresses in dental crowns

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13.1 Overview of finite element analysis

13.1.1 Basic description

Finite element analysis (FEA) was originally developed within the aircraft industry (Turner *et al.*, 1956) and has since become widespread in engineering, ranging from the estimation of thermal stresses in reactor vessels to structural analysis in civil engineering. In dentistry, FEA was shown to provide reliable information concerning stress distribution in a tooth as far back as the 1970s (Farah *et al.*, 1973). The FEA method consists of dividing the geometry of a structure into a finite number of elements, elements with mechanical properties that are relatively easy to describe. The geometry of these small elements can be bars, wedges, tetrahedrons or other shapes. The approximation is made that the properties are uniform for a specific element. On this basis, the stress distribution, for example, in an FEA model of a tooth will not change gradually, but in steps. The classical theories of mechanics, together with the division of the geometrical shape into a finite number of elements, create the possibility of mathematically determining the stresses in a structure, resulting from loads that are applied to the same structure. The elements are connected by nodes at their corners. The displacement of a specific node due to load on the structure can be calculated for each element connected to the node. The displacement is a function of the force on that element.

Since it is one node, all calculated displacements of the node, each resulting from the function of the connected elements of the node, must be the same. This results in a number, n , of equations combined with n unknown displacements. The computer is used to solve this mathematical problem.

13.1.2 Necessary computing capacity

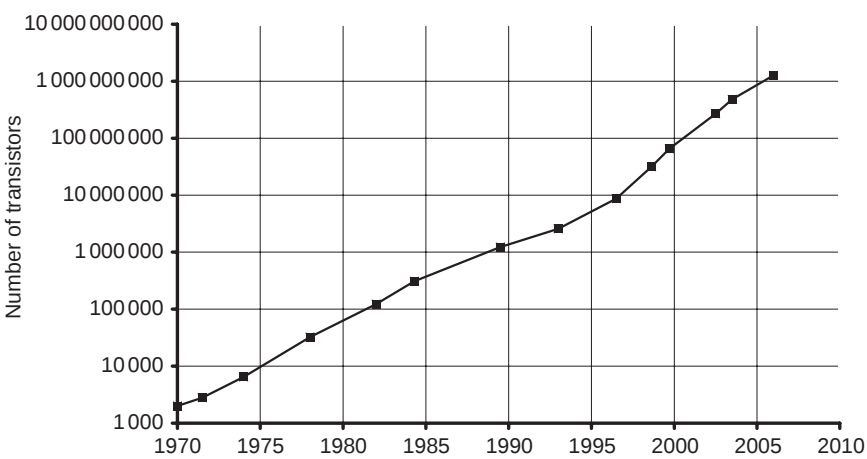
Nowadays, the impressive development of computing power, even with standard personal computers, makes it possible to calculate accurately

the development of stresses in complex geometries, like a prepared tooth restored with a crown, for example. According to Moore’s law (a 40-year-old prediction by Gordon Moore, cofounder of the Intel Corporation) computing capacity is doubling approximately every two years (Fig. 13.1).

The use of multi-layer ceramics, in combination with an ultra-thin adhesive cement layer whose mechanical behaviour is associated with shrinkage problems, makes an analysis of the mechanical response occurring in dental restorations complex. This implies that three-dimensional (3D) FEA is practically the only way to obtain a meaningful solution to the calculation of stress and strain fields that are created in the structure, and which are built up in various locations simultaneously. The approach used to model the shrinkage of materials during setting, as with that used to model the simulation of the behaviour of luting cements during setting, is solved using an iterative process (de Jager *et al.*, 2005b). The computing time required for such an iterative process is still considerable, even for a personal computer with a high specification.

13.1.3 How to validate the results

The solution of the equations is an exact solution. However, the formulation of the problem and the data used could give a discrepancy between the physical reality and the FEA leading to approximate solutions. The function used for the stress due to the load on the elements might be too simple to



13.1 The development of computing capacity, illustrating Moore’s law.

represent the real stress in the element and the use of a finite number of elements leads to such an approximation. For these reasons, it is necessary to validate the model. First, a simple method of validation of the FEA results is to compare the stresses or deformation on the geometry due to the applied load with the results of loading on similar geometries or with the anticipated results. When the results are similar or as expected one might assume the results to be correct. In order to judge if the model is of sufficient detail, with respect to the type of elements used and the number of elements, most FEA programs are able to make posterior error estimates for every output item, which guarantees a solution of high quality. An alternative approach for validation is to refine the model by increasing the number of elements and using elements with a more sophisticated element description, for example with the use of midside nodes. The solution is of sufficient quality if these changes do not result in a substantial change in the solution.

13.1.4 Future developments in the application of finite element analysis

Although there are already many high technology applications in dentistry – such as intra-oral cameras, digital cavity and pocket depth meters, bite impression systems, CAD-CAM systems (computer aided design and computer aided manufacturing) and FEA – the integration of the different features is lacking.

A breakthrough for integral computer applications will allow these technologies to be combined. It might be expected that in the near future an indirect restoration will be made based on an intra-oral scan of the geometry of the preparation and surrounding environment inclusive of the opposing teeth. Hereafter, this information can be transmitted to a CAD program. The CAD program is used to design the final shape of the crown restoration based on a standard shape selected from a library, while the program designs the contact surface for optimal contact with the opposing dentition. In fact, the CAD program designs the crown including a cement layer. Before manufacturing the restoration, the design can be transmitted to an FEA program to evaluate the stress distribution and to identify possible intrinsic weaknesses. More specifically, the FEA is executed to ensure that there are no stresses surpassing the stress limits for the loading conditions on the specific tooth, indicating the points to be modified in the CAD design. In this way a non-destructive test of the design of the restoration before production is performed. Finally, the CAD design can be transmitted to a CAM program for automated production of the restoration.

13.2 Finite element models for indirect restorations

13.2.1 Stress analysis in the 1950s

The determination and improvement of the mechanical strength of dental structures has been the subject of much study since the mid-point of the last century. The stress analysis method used in those days was a well-recognized engineering technique based on the change of reflection of light due to stresses in the material – the photoelastic method. The first publication of these analyses in dental research appeared in 1949 (Noonan, 1949). Three-dimensional composite studies based on photoelastic analysis have been limited because of the complexity involved in the determination of the complete state of stress in a three-dimensional irregularly shaped structure such as a restored tooth.

13.2.2 The coming of finite element analysis

The FEA method was introduced to dental research in the 1970s (Farah *et al.*, 1973). Models of a first molar with full gold crown preparation were made. The axi-symmetric two-dimensional (2D) model consisted of 348 elements and was built by describing the coordinates of each nodal point in a computer program. The FE approach provided a more detailed evaluation of the complete state of stress in the model. Two-dimensional models were still being used in the 1990s (Kamposiora *et al.*, 1994), because of the disadvantages of constructing 3D FE models that were more complex and the number of elements that were required for these models was beyond the operating capacity of many computers at that time. Despite the difficulties of working in three dimensions, in 1990, a simple 3D model of glass-ceramic dental crowns consisting of 586 nodes and 456 elements was developed (Hoiijatje and Anusavice, 1990). In 2000, other researchers (Palamará *et al.*, 2000) built a 3D model of an intact, non-carious premolar. In order to construct this 3D model, a tooth was cleaned, dried and embedded in an epoxy resin block, which was sliced in 25 transverse sections. Each section was stained, photographed and digitized.

The digitized sections were used to recreate a 3D geometry in the FE software. A simpler method to make 3D models is to rotate a 2D model (Güngör *et al.*, 2004) if the geometry is symmetric. In order to create a FE model that will possess the necessary detail to reproduce the complexity of structures within dental restorations, the modern technology of CAD-CAM can be used (Ausiello *et al.*, 2001; De Jager *et al.*, 2005a). With CAD-CAM a CAD design is used in a computer-driven milling machine to realize the desired shape using the CAD information. The conversion of the CAD model into an FE model is not simple and it is still necessary to make a

conversion of the CAD model, to make it possible to read the model into the FEA software. In the future, it would be expected that CAD (design) software would provide routines to complete this task automatically or at least interactively.

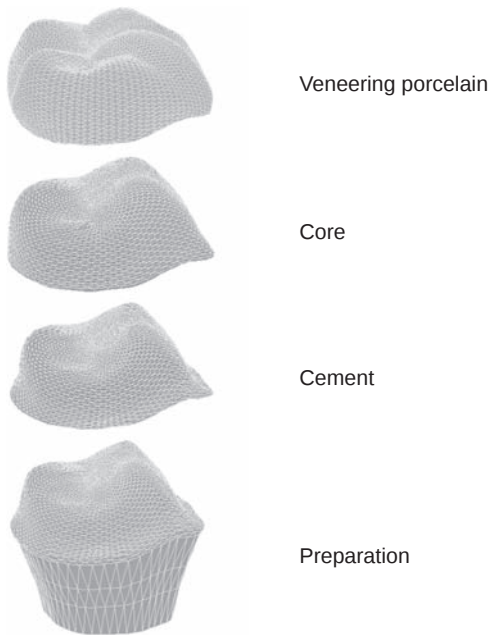
13.2.3 All-ceramic dental crown model

In order to show the potential of using FEA for modelling of the stresses in indirect restorations, we will present an example of an FEA study of all-ceramic dental crowns using the CAD model, with the objective of establishing design parameters for dentists. For the study, the CAD models of the crowns of three patients with crowns for posterior tooth 46 are prepared for a 3D FEA using a commercial package. The FE modelling and post-processing was carried out with FEMAP software (FEMAP 9.2, USG Corp., Plano, Texas, USA), while the analysis was done with NX Nastran software (NX Nastran, USG Corp.). The crowns consist of a core made of a pressed, high-strength, alumina-based porcelain, veneered with a leucite-free glass ceramic.

The models consisted of between 50 000 and 65 000 parabolic wedge and parabolic tetrahedron solid elements. Wedges are more sophisticated elements necessary for the thin cement layer whereas with the tetrahedrons it is easier to mesh geometries. The FEA using meshes of this size can be processed quite adequately with the increased computing capacity available, even using normal modern personal computers with sufficient processor power (3 GHz) and working memory (2 GB). A crown with a chamfer knife-edge preparation and a uniform cement layer thickness (crown 1) was compared with a crown with a chamfer and collar preparation and a uniform cement layer (crown 2). For a third crown, with a chamfer and collar preparation, a cement layer that varied from 0.025 to 0.140 mm was compared with the same model with a uniform cement thickness design. The final model consisted of two ceramic layers (veneer and core), a cement layer and the prepared tooth (Fig. 13.2).

There were three stress outputs calculated.

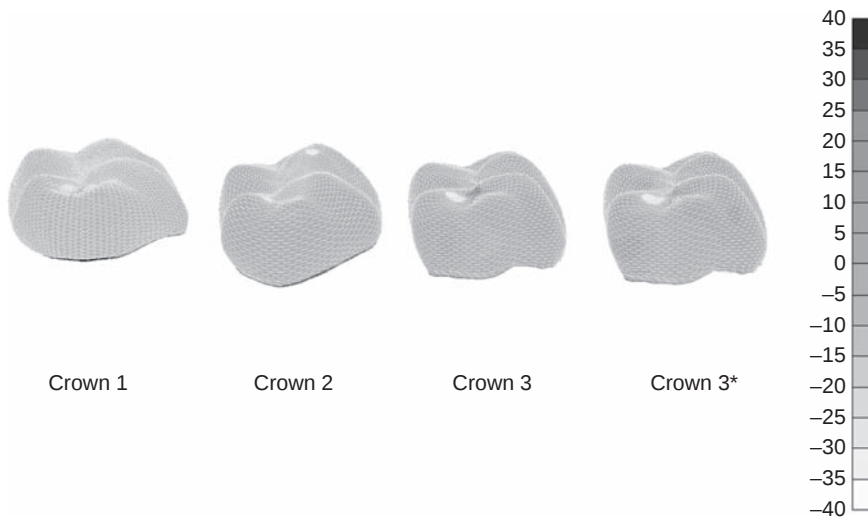
- *Stresses due to bite forces.* The bite force was distributed uniformly on the points of contact in occlusion, perpendicular to the surface. The resulting vertical (z) component was 665 N.
- *Residual stresses due to the difference in thermal expansion coefficients of the two layers forming the crown.* To determine the residual stresses after production of the crown, caused by the difference in the coefficient of thermal expansion of the two materials (the core material and the veneering porcelain), the temperature–expansion diagrams of these materials were used to calculate the expansion.



13.2 The layers comprising the FEA model.

- *The influence of shrinkage of the cement.* The setting of resin composites is a complex and time-dependent process, during which material properties undergo a dramatic change in a relatively short period of time. To determine the stresses due to shrinkage of the cement during hardening of the resin composite a time-independent non-linear elastic-plastic material model was used (De Jager *et al.*, 2005b).

The stresses caused by the variables were calculated separately, then the three outputs were combined using the linear combination facility, which recalculates the combined stresses based on the output vectors of the linearly combined components (Fig. 13.3). The crowns are shown in distal-mesial view, showing that the highest stress at the cervical surface is located at the distal-lingual side. The relatively high principal tensile stress at the cervical surface is caused by the different influences, where the shrinkage stress of the cement layer, in particular, plays an important role. The use of multi-layer ceramics in combination with an ultra-thin adhesive layer, whose mechanical behaviour is largely associated with shrinkage problems, implies that 3D FEA is the only practical way to obtain a meaningful description of the crown under load, in which all of these processes that are having an



13.3 The stresses (in MPa) at the cervical surface in distal-mesial view.

influence on the stresses arising in the crown take place simultaneously. As can be seen from the figures, the highest stresses are found in the crown with the chamfer knife-edge preparation (see crown 1, Fig. 13.3). The relatively high principal tensile stress at the cervical surface is strongly influenced by the shrinkage of the cement. The principal tensile stress at this location is mainly tangential.

Fracture could initiate at the cervical surface in spite of the lower FEA calculated stress, because stress intensities can be high due to shape and size factors, as well as increased susceptibility to flaw formation at the crown margins. In the FEA models the veneering porcelain does not end exactly at the margin, which is usually the case with production crowns; otherwise the shrinkage of the cement could have resulted in still higher stresses due to the more unfavourable loading conditions in those circumstances on the veneering porcelain. Although crown 3 has a chamfer with collar preparation due to imperfect preparation at the distal-lingual side, the shape of the preparation in this location is rather like a knife-edge. It is still too labour intensive to evaluate the stresses for every crown that is produced in a clinical setting, but with studies such as these, specific design rules can be developed that should help dentists to prepare better restorations. For example, using a chamfer with collar preparation instead of having a knife-edge at the preparation line and to use uniform cement layer thicknesses.

13.3 Challenges involved in deriving material properties for finite element analysis

13.3.1 Material properties in general

For homogeneous, linearly elastic, isotropic materials – without considering time – or temperature-dependent processes – the only two material properties needed as input for an FEA are the Young's modulus and the Poisson's ratio. These properties are explained in Fig. 13.4. The Young's modulus E is, according to Hooke's law (Timoshenko and Godier, 1980):

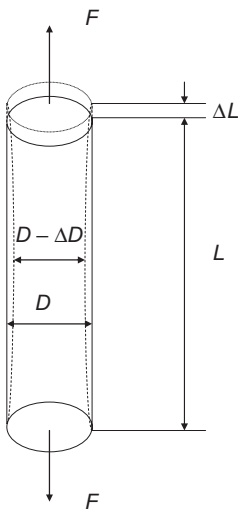
$$E = \frac{\sigma}{\varepsilon} \quad [13.1]$$

where the normal stress σ is $\sigma = F/[(\pi/4)D^2]$ and the strain ε is $\varepsilon = \Delta L/L$. The Poisson's ratio ν is:

$$\nu = \frac{\Delta D/D}{\varepsilon} \quad [13.2]$$

where D is the diameter and the strain ε is $\varepsilon = \Delta L/L$.

These properties can be found in the literature or can be determined with specific test configurations. However, materials properties are not always homogeneous, linearly elastic and isotropic, and can be time-dependent. An example of a non-isotropic material is fibreglass-reinforced resin composite.



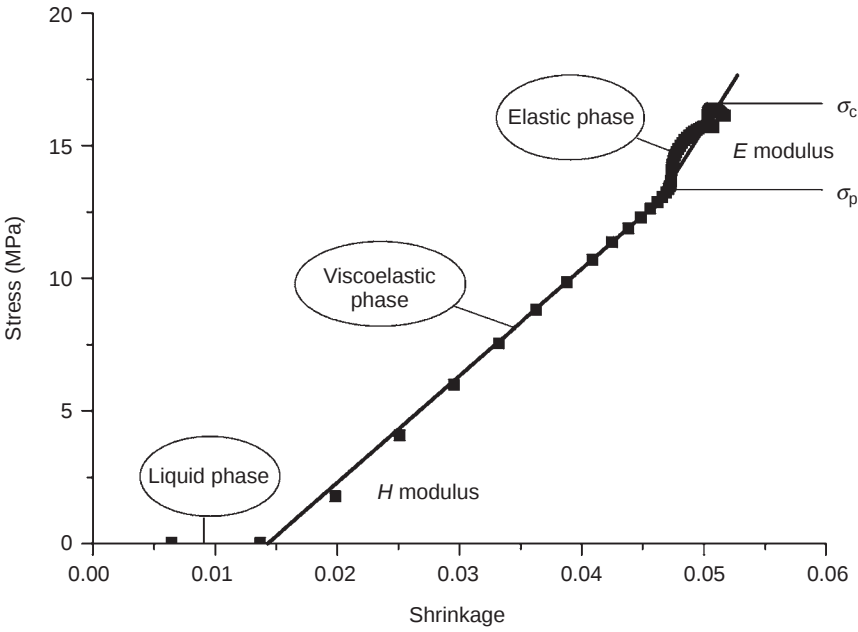
13.4 The change in diameter with axial stress.

The Young's modulus and Poisson's ratio for this material are different in the length direction of the fibres compared with the properties in the perpendicular direction. These variations can be modelled by most FEA programs.

A relevant example of a time-dependent material property is the shrinkage of the cement layer. Knowledge of the development of polymerization shrinkage in these layers, and of its distribution and height, is of key importance for a reliable risk assessment of the durability of dental indirect restorations. The observation of this process is difficult experimentally, as the setting of resin composites is a complex time-dependent process, during which material properties undergo a dramatic change in a relatively short period of time. However, the setting reaction for resin composites is well described in the literature (Dauvillier *et al.*, 2001).

On the other hand, an FEA-based algorithm for the modelling of the setting reaction is unavailable, so powerful FEA software algorithms, applying a multi-step approach, may be required. These are not available in most standard software packages. In the literature many FEA studies are reported where the setting process is simplified to a single-step process in which the thermal expansion mode of the FEA software is used to mimic the shrinkage, assuming pure elastic behaviour of the restorative material (Ausiello *et al.*, 2001, 2002). Winkler *et al.* (1996, 2000) divided the curing process into several steps with increasing depth of cure, and assuming single-step elastic behaviour for the model system. For this approach, during FEA processing, parts made of the material are simply scaled down in all directions (x , y , z) according to their free linear shrinkage. Consequently, deformation and stress will now occur, because the part that undergoes shrinkage remains bonded to the fixed surfaces. The single-step approach assumes that all deformation develops at the same rate, which is certainly not true in many dental restorations. So the multi-step approach requires sophisticated software and difficult material property determination, while the single-step approach can only be used in a very limited number of cases. Nevertheless, it may be possible to use existing FEA features to mimic the complex process of the development of setting stress in a rather simple way. Most standard FEA software has the capability of dealing with elastic-plastic behaviour.

This means that the material may be characterized by two linear stress-strain relations: one characterizing the elastic part, the Young's modulus E , and a second approximating the portion beyond the elastic limit, i.e. the hardening modulus H . The transition between the two moduli is the amount of strain marked by the change in the stress-strain relation rather than a point in time marking the onset and progression of the setting process (see Fig. 13.5). The setting process can be expressed as a stress-shrinkage plot, which is time-independent and consists of a liquid phase where the



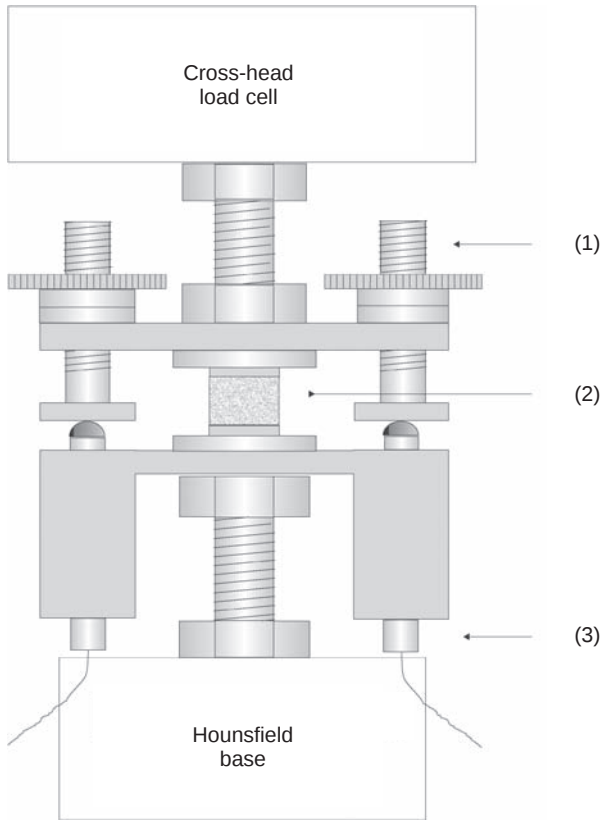
13.5 Relation between contraction stress σ and shrinkage ϵ during hardening. σ_c , cement point; σ_p , transition point.

materials shrink without the development of stress, a visco-elastic phase where the shrinkage partly leads to stress formation and partly is relieved by viscous flow, and an elastic phase where all shrinkage is transformed to stress.

13.3.2 Model of the shrinkage of the cement layer

There follows an example of how to determine this property for the dual-curing luting cement, RelyX ARC (3M ESPE, MN USA). To assess the stress–shrinkage relation of the material for the early stage of setting, bonded luting cement discs were cured in a simple, straight-forward tensiometer test configuration (Fig. 13.6). Any axial displacement of the adhesive surfaces was determined with the aid of an extensometer consisting of two inductive probes. The specimens were tested in two conditions: one in which the curing contraction of the specimens was hindered (strain = 0) and one in which the specimens were free to contract in the axial direction (unhindered condition; load = 0).

In the hindered condition, the moving cross-head compensated automatically for any axial displacement of the adhesive surface, to maintain the



13.6 Test set-up with (1) adjustment bolts, (2) sample and (3) inductive probes.

original sample height; in the unhindered condition, the moving cross-head compensated for any load recorded by the load cell, to maintain a zero load on the specimen. In this way the specimen was free to contract. In the unhindered configuration, linear shrinkage data were obtained, while in the hindered configuration setting stress data were gathered, both as a function of setting time. The combination of both data sets enables the determination of the setting stress–shrinkage relationship. To obtain the elastic strain as a function of setting time, periodically loaded, strain cycles were performed during execution of the test in the hindered configuration. A small amount of compliance in the test set-up, during loading, is inevitable, and this may have a relatively large influence in very thin cement layers. For this reason all displacement values measured should be corrected for the compliance of the test set-up. The data obtained are used

to calculate the Young's modulus E and the hardening modulus H (Fig. 13.5). The initiation of stress development and the progression of stress development in the hindered condition are equated to the onset of visco-elastic behaviour and of elastic behaviour, respectively. The data obtained in this way can be used as input for a time-independent FEA model. The data are tested in a simple FEA model, which represents the test set-up. The results show that it is possible to predict contraction stresses with these parameters.

13.4 Clinical significance

13.4.1 Dental decay

Less than 3% of the early hominid *Paranthropus robustus*, who lived between 1.8 and 1.5 million years ago, had caries (Grine *et al.*, 1990). Most likely, changing food habits would have contributed to the fact that later hominids developed more caries, so that in relatively modern times, individuals are in continuous need of prosthetic reconstructions.

In the Louvre in Paris, a dental appliance is on display that dates from between 400 and 330 BC and is attributed to the Phoenicians, and which may be considered to be the oldest known fixed partial denture. So, little has changed and today mankind is still in need of prosthetic reconstructions, despite increased efforts to prevent dental decay. Nowadays, modern production techniques and the materials available to practitioners make the production of reliable restorations possible. However, the failure of restorations is far from unknown, especially when placed in the posterior region. Various factors are attributed to this phenomenon. One of the most important ones may be the materials used, and the shape of the restoration and the cement layer.

13.4.2 Guidelines for dentists

Ideally, we want to provide guidelines for all types of restorations so that dentists following these guidelines will have good results. For restorations that are produced manually (direct restorations), design weaknesses can hardly be predicted, as the design of the restorations is an operator-dependent property.

However, for computer designed and manufactured (CAD-CAM) restorations, the design of the restoration and of the prepared tooth is available digitally, making stress analysis and failure prediction possible. This analysis can be done successfully using the FE method. For the clinical interpretation of the results from FEA studies of crowns, it should be taken into account that the crown, placed clinically, will probably differ in some respect

from the FE model. One possible error can be introduced following the transformation of the CAD model into the FE model. A further error could occur during crown production. For instance, the glazing of crowns will round off sharp edges; this is not included in the design but could be simulated using smoothing features within the FE modelling software. Furthermore, the crown might differ from the FE model through contact damage flaws and also the surface roughness of the porcelain will affect the strength of the material (De Jager *et al.*, 2000). FEA of crowns has shown that the critical area of the crown is not the occlusal surface, just as the analysis of clinically failed crowns has shown that failures do not initiate from flaws on the occlusal surface (Kelly, 1999). During loading, restorations develop features that have come to be called 'wear facets'. Clinicians recognize that wear facets are usually not point contacts, as used in FE studies, but have dimensions of up to approximately 3 mm in diameter (DeLong, 2006). This effect will result in a distribution of bite forces over a greater area, which will lower the stresses. In addition, the number of points of occlusion influences the development of stress within and under the occlusal surface layer.

For all-ceramic crowns, the thermal contraction mismatch of the core and veneering porcelain might be expected to increase the maximum tensile stress in the veneering porcelain at the core-veneer interface. Ceramic materials do have a much higher strength when in a state of compression than under tensile stresses. For this reason, a thermal contraction mismatch is intended to subject the veneering porcelain to such a state of compression. However, FEA studies have shown that in contrast to this, in some regions of the interface, the rather complicated shape of a crown causes tensile stresses in the veneering porcelain. In addition, clinically, Cerestore crowns (Ceramco, Johnson & Johnson) have shown failures mainly from sites located at or near the core-veneer interface (Thompson *et al.*, 1994). Kelly *et al.* (1989) analysed Dicor crowns (Corning Inc, New York, USA) that failed clinically at the cementation surface. The stresses found through FEA in this region would have led to a high failure probability taking into account the level of maximum strength of the materials used in 1989. However, the strength of the core materials has since been improved considerably and nowadays failures should not occur at the cement interfaces. Apparently, in FEA studies, no relationship has been found between the maximum tensile stress in the core at the cementation surface and the occlusal thickness, nor between the maximum tensile stresses and the shape of the cement layer. This is in accordance with the literature for occlusal thickness (Hojjat and Anusavice 1990; Proos *et al.*, 2003a) and for the cement layer (Sjögren *et al.*, 1999; Proos *et al.*, 2003b).

We have seen earlier in this chapter (Section 13.2) that results from FEA studies are able to provide general design rules for the design of dental restorations, e.g. knife-edges at the margin should be avoided and for a

chamfer with collar preparation with imperfect cutting at the distal-lingual side the preparation can be rather like a knife-edge. Clinicians will recognize the difficulty in fabricating perfect preparations, especially in the lower jaw on the lingual side. This can be found in the literature (Begazo *et al.*, 2004); from their study, they observed that nearly all preparations are likely to have one or more imperfect locations, most of these being in the lower jaw. The results from Section 13.2 also show that the stresses in non-uniform cement layers are considerably higher than in uniform cement layers. The stresses in the non-uniform cement layer are higher than the bond strength (Cobb *et al.*, 1999; Braga *et al.*, 2000). Indicating that the application of non-uniform cement layers in the clinical situation results in a considerable risk of debonding. In general, results of FEA studies can provide clinicians with good guidelines to follow in daily practice. In the future, FEA of restorations produced by CAD-CAM should provide a means of evaluating single restorations in a non-destructive manner to check that the design is optimized before production of the restoration.

13.5 Summary

Mankind is still in need of prosthodontic restorations despite an increased effort to prevent dental decay. Nowadays, modern production techniques and materials available to practitioners and dental laboratories make the manufacture of reliable restorations more likely. However, indirect restorations are still known to fail, especially when placed in the posterior regions of the mouth. Various factors contribute to these phenomena, and it may be argued that the most important ones could be the materials used, the shape of the restoration and the cement layer. The determination and improvement of mechanical strength of dental structures has been the subject of study since the latter half of the last century, although it is now better appreciated that other measures can be more important in some cases, i.e. fracture toughness and fatigue strength. The method of stress analysis used in the past, was a well-recognized engineering technique based on the change of reflection of light due to stresses in the material. FEA was originally developed in the aircraft industry and has proven to be a very useful tool for dentistry also, providing reliable information concerning the stress distribution in a tooth since the 1970s. In the FEA method the geometry of a structure is divided into a finite number of elements, with relative ease, to describe mechanical properties; thus creating the possibility of calculating the stresses in a structure mathematically. In order to make long-lasting restorations it is advisable to have specific design rules for the production of these restorations. For direct restorations, design weaknesses can hardly be predicted as the design of the restoration is an operator-dependent property. However, for computer designed and manufactured

indirect restorations (CAD-CAM), these parameters, as well as those of the preparation, are digitally available, making stress analysis and failure prediction possible.

This analysis can then be done using the FE method. For homogeneous, linearly elastic, isotropic materials, without time- or temperature-dependent processes, the only two material properties needed as input for the FEA program are the Young's modulus and the Poisson's ratio. These properties can be found from the literature or determined from specific mechanical test configurations. However, material properties are not always homogeneous, linearly elastic and isotropic, and can also be time-dependent. Even so, the most modern FEA programs can cope with these demands.

Section 13.1 provided a historical background of the development of FEA in dentistry and its potential in this area has been made possible by the developments that have taken place in computer processor speeds and memory capacity, even with standard personal computers. A short explanation was given of the basic principles of FEA, extended to the possibilities and limitations of the method and the necessity of validating the results. Section 13.2 explained how FE models for indirect restorations can be realized and how this development has come about in recent years. An example was given of an FEA study of all-ceramic dental crowns. The CAD models of the crowns of three patients with crowns for posterior tooth 46 were transformed for analysis in a 3D FEA program (FEMAP 9.2, USG Corp.).

The results showed that the tensile stresses in crowns with chamfer knife-edge preparations might put the integrity of the current dental ceramic materials at risk, while a non-uniform cement layer thickness could result in stresses exceeding the bond strength, and differences in thermal expansion of the two ceramics could increase the tensile stresses in the veneering porcelain. This should lead to rules for the manufacture and clinical handling of crowns, e.g. using a chamfer with collar preparation instead of a knife-edge at the margin and to use uniform cement layer thickness for these restorations.

In Section 13.3, material properties to be used in FEA studies were discussed and an example was given of how time-dependent material properties such as the shrinkage of the cement layer can be incorporated into the models. The knowledge of the polymerization shrinkage of these layers is of major importance for a reliable risk assessment of the durability of indirect dental restorations. It is shown that the setting process can be expressed as a stress-shrinkage plot, which is time-independent. Section 13.4 dealt with the clinical significance of FEA applied to dentistry. It was explained that for a clinical interpretation of the results of FEA studies, e.g. in dental crowns, it should be understood that the clinical crowns might differ from the idealized FE models. Possible errors are introduced by transformation

of the CAD model into the FE model, or are introduced during the physical production of the crowns. Glazing of crowns will round off sharp edges; this is not included in the design but can possibly be simulated using smoothing features provided within FEA software.

Furthermore, the crown could differ from the FEA simulation, as a result of contact damage flaws and the surface roughness of the porcelain will affect the strength of the materials. Even so, the results of FEA studies are in line with results found in the clinical situation. This understanding makes it possible to develop general rules for restorations that can be followed by clinicians.

In the not too distant future, for an indirect restoration, with the high technology applications already available in dentistry – such as intra-oral cameras, digital cavity and pocket depth meters, bite impression systems, CAD-CAM systems and FEA – a breakthrough for integral computer applications will become possible. In the integrated sequence of imaging, modelling and testing, FEA can provide the control that there are no stresses surpassing the stress limits under the loading conditions of the specific tooth, indicating eventually the points to be corrected in the design. In this way, non-destructive testing of the design of the restoration, before production, can be performed.

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Testing the performance of dental implants

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14.1 Introduction: an overview of systems and their development

14.1.1 History of dental implants

The history of dental implants is inextricably linked to the process of tooth loss, either through disease or trauma. Evidence from ancient civilisations has reported the use of many materials including wood, seashells, stone and carved ivory. Apart from artificial materials, transplantation of teeth from animals or other humans also commonly occurred. The aim in these situations was to create a functional connection to the new site by re-establishing the periodontal ligament. In reality, the antigenic nature of the transplanted tooth led to a host immune response that either rejected the tooth or led to ankylosis with subsequent root resorption leading to failure and loss (Powers and Sakaguchi 2006).

It is thought that the first reference to a modern-style manufactured implant occurred early in the nineteenth century when J. Maggiolo described a tooth-root-shaped implant cast from 18-carat gold. These were inserted into fresh extraction sockets. Following a healing period, a porcelain crown could then be constructed to attach to the 'new root' (Ring 1995). Further developments in both metallic and root-shaped implants have occurred mainly within the twentieth century in tandem with developments in dental materials. This period also marked the advent of experimental implantology as well as research into tissue biocompatibility. Implants were manufactured from chrome alloys and from Vitallium due to their electrolytically passive nature. Strock, in 1939, first attempted to change the shape of a dental implant from that of a tooth-root by using Vitallium to construct an implant with threads resembling a wood screw (Spiekermann 1995). Other implant materials used included ceramics, sapphire, vitreous carbon and even methyl methacrylate. All of the above-mentioned materials had one thing in common: their success and survival rates were greatly variable and unpredictable. Although some of these could function well for several years,

many display failure from infection or by fibrous encapsulation leading to loosening and eventual rejection. It can be considered that there are two elements to replacing a tooth: material for the replacement of teeth and some form of attachment mechanism into the jaw bone (Worthington *et al.* 2003). Teeth are secured into the jawbone by the periodontal ligament (PDL). This complex also has the ability to act as a shock absorber and have a sensory role. The PDL can also mediate bone maintenance and influence tooth movement. Historically, the establishment of such a complex around implants was seen to be the ideal environment. What is of importance, however, is that the implanted material is physically and biologically compatible with alveolar bone and that it has some form of retention mechanism to that bone.

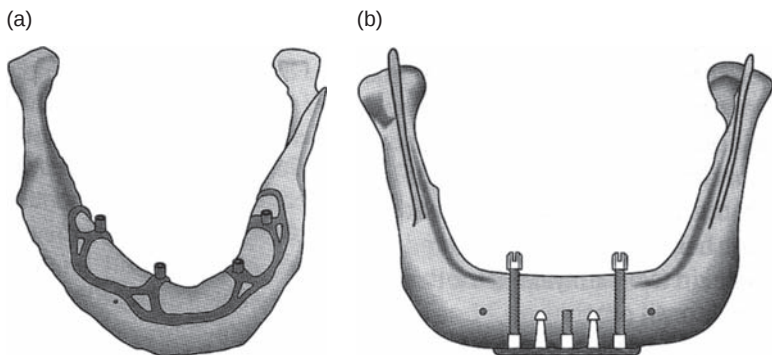
It was an accidental discovery, during experimental work carried out by Professor Per-Ingvar Brånemark in Sweden that has led to the modern era of implant dentistry based on osseointegrated techniques. In the 1950s Brånemark, a Swedish orthopaedic surgeon researching bone growth using vital microscopy, observed the fusion of his titanium chambers to bone in the femur of the rabbits under observation. As the aim of his studies was to observe living bone, these chambers had been introduced into bone using gentle surgical techniques. When attempts were made to remove these chambers following the killing of the animals, it soon became apparent that these structures had bonded irreversibly to the living bone. He then went on to repeat the effect and subsequently demonstrated that certain conditions were necessary to allow titanium to fuse into living bone. Brånemark named this phenomenon 'osseointegration' and started to look for applications of its use within the field of dentistry. Osseointegration was defined as the direct structural and functional connection between ordered living bone and the surface of a load-carrying implant (Brånemark *et al.* 1987). It is now known that a structural connection does not exist and that implants are secured by anchorage created by the close apposition of bone to the implant surface. As such it is more like the phenomenon of ankylosis. Brånemark together with his co-workers then went on, over several years, to develop a two-stage implant system using titanium threaded implants. The first implantation of titanium screws was carried out in an edentulous patient in 1965. There then followed a period of controlled, prospective clinical studies to assess the survivability of the implants.

The prognosis for implant-retained oral superstructures had come to be regarded with scepticism until Professor Brånemark finally reported the success of the osseointegrated method in 1978 at the Toronto Conference on Osseointegration in Clinical Dentistry. This was followed in 1981 by the publication of a 15-year initial study with the installation of 2768 implants. Previous to this seminal work, no objective complete experimental analysis had been carried out to demonstrate the biological pre-requisites for

permanent anchorage of a dental prosthesis in the jawbone (Adell *et al.* 1981). It is worth noting that Brånemark was not the only investigator who had focused on the role of titanium in modern implant dentistry. In 1981, Professor André Schroöder in Switzerland introduced a titanium plasma-sprayed, one-piece trans-mucosal screw based on previous work carried out by Dr Ledermann. The research accompanying this development was only published in the German literature and hence did not initially gain as much recognition as the work of Brånemark. Of note was that both parties had demonstrated, with differing protocols and designs, the ability for dental implants to be predictably secured within alveolar bone and both focused their efforts into understanding the process by which this occurred.

14.1.2 Types of dental implants

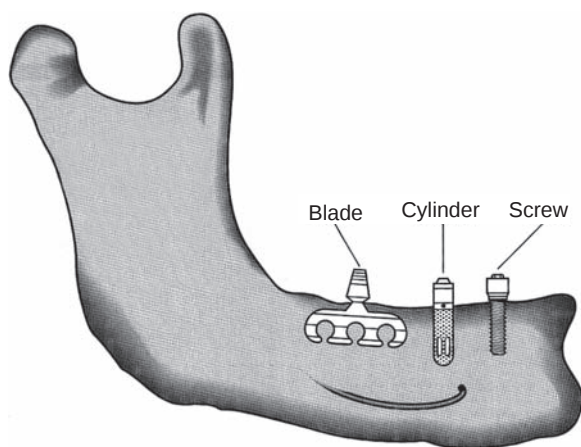
Historically, dental implants have been classified into categories based on the method of surgical implantation. The three types of implants used over the last 50 years are the subperiosteal, transosseous and the endosseous. The subperiosteal implant consisted of a metallic frame designed to rest on the alveolar bone beneath the periosteum. These frameworks were custom-made on models made from an impression of the edentulous jaw taken with the muco-periosteum surgically reflected. Cast from a cobalt-chromium–molybdenum alloy, they were subsequently inserted at a second surgical procedure. Such frameworks had posts that penetrated the mucosa into the mouth and were commonly used to support overdentures (Fig. 14.1a). Transosseous implants included the transmandibular staple. The application of



14.1 *a* Subperiosteal implant. These were usually cast in cobalt-chromium (reprinted from Worthington *et al.* (2003) with permission). *b* Trans-mandibular staple implant. Illustration shows the general design of a staple bone plate (reprinted from Worthington *et al.* (2003) with permission).

this implant was limited to the anterior mandible and consisted of a plate with post projections. The device was surgically placed on the inferior border of the mandible through an external approach. Some of the posts were then inserted into the lower border of the jaw while others were designed to penetrate through the bone and project through the mucosa covering the edentulous ridge (Fig. 14.1b).

The essential difference with the endosseous form of implants is that the implant is embedded into the jawbone as opposed to resting on it. It also commonly only penetrates one cortical plate. Three basic types exist (Fig. 14.2). The ramus frame consists of a custom-made supramucosal framework that is inserted into the mandibular symphysis and into each ascending rami. The blade implant consists of a flat plate often with a coating of hydroxyapatite or with fenestrations. Due to its slender body design the implant can be placed in bone with limited width. Insertion consists of the preparation of an accurate trough in the jawbone into which the implant would be snugly inserted to achieve primary stability. By far the most common type of endosseous implant is the root form variety. Both cylinder-shaped and screw thread varieties exist. The placement of a root form implant is based on drilling an exact hole into the jawbone using drills matched to the implant size. Cylinder-shaped implants can be inserted using a 'press-fit' technique. In the case of screw thread implants either the osteotomy site can be tapped or the implant itself has self-tapping features allowing it to be inserted by rotating it into place. These implants are positioned either flush with the surface of the bone



14.2 Endosseous implant designs. Currently the most common type is the root form endosseous variety (reprinted from Worthington *et al.*, 2003, with permission).

or slightly protruding. The internal chamber of the implant is usually threaded with locking features to allow for a tooth or teeth to be connected to it via an abutment. The latter is usually screwed through the mucosa into the body of the implant. The predictability of the root form endosseous screw thread implant has made it the most commonly used implant since 1986 and the remainder of this chapter will focus entirely on this type of implant.

14.1.3 Osseointegration

Osseointegration is now formally defined as the close approximation of bone to an implant material and can only be achieved if bone is viable. It has been stated that in real terms the process is that host bone responds – in a safe, predictable and versatile manner – to surgery and implant placement into a sterile wound, with a healing cascade leading to interfacial osteogenesis and mechanical stability of the implant. The crucial point is that the bone and marrow around an implant must heal as highly differentiated tissues and not a slow differentiation scar tissue.

Implant placement is a multi-dimensional problem associated with the insertion of a foreign device into the body. Brånemark and subsequently Albrektsson stated that the successful outcome of any implant procedure is dependent on the interrelationship of the various components of an equation that include material biocompatibility, implant surface, implant design, the surgical technique and patient-related factors associated with the status of the implant site and the loading conditions endured by the implant. With regards to the latter, not only is it important to consider the magnitude and direction of loads sustained on a dental implant in function but also the period of time that the implant is left to heal unloaded.

The choice of material for an implant has to be based on many different requirements including mechanical strength, machinability and topography. One property of prime importance is that of biological compatibility. This biocompatibility needs to occur on both a macroscopic and microscopic basis. Within a biological environment, a variety of responses can occur with a biomaterial with, at one end of the scale, reactive pathological processes leading to corrosion products. On the other hand, passive reactions are possible mainly due to passivated surface oxides (Stanford *et al.* 1994). The current trend towards titanium is based on a general consideration of the desirable properties mentioned above. As a lightweight metal it offers a high strength-to-weight ratio, with good fatigue resistance and the ability to be corrosion resistant due its tenacious surface oxide which provides a stable interface for bone deposition. Early implants were based on a single design concept, prepared into a screw-type form of varying lengths from commercially pure titanium without any surface

modifications and commonly known as a machined surface implant. Historically, high clinical success rates have been achieved by screw-type implants with a machined surface. However, these implants have also shown an increased failure rate in compromised sites of low bone density and reduced vertical bone height where short implants have been used. In recent years, differing surface configurations have been proposed aimed at improving the cohesive properties of the implant–abutment interface, maximising load transfer in an effort to lengthen the service life of the construct. Considerable effort has been spent in developing surfaces that will also accelerate the process of bone apposition to allow healing times to be reduced. Anatomically, it is also known that differences exist in the type and density of bone in different areas of the jaws. This can also be compounded by patient-related conditions that can compromise the response to healing. Implants have been coated with hydroxyapatite (HA) on the basis that this material replicates the inorganic phase found in tooth and bone, and hence better bonding would be expected. Current methods of HA application have, however, led to considerable changes in its *in vitro* dissolution behaviour, with the major clinical limitation of the inability to predict and maintain bond strength of the coating to the metal. The long-term stability of many HA-coated implants is therefore uncertain. Surface-roughened implants, sometimes also known as textured implants, have also been implemented into clinical practice. In an effort to improve long-term fixation, increasing its surface roughness can modify the topography of an implant. It is known that the response of osteoblasts to roughened surfaces is more favourable and that there can be better interlocking between implant and bone at the micrometric level (Natali 2003). Roughened surfaces can be created by blasting with a variety of materials, including titanium dioxide, or grit, and also by surface treatments including sand blasting and acid etching. These methods are used to erode the substrate, forming an irregular surface with pits and depressions that vary in size and shape depending on the blasting conditions. An optimal surface has been defined as one with roughness created by surface pits or holes ranging from 1.5 to 5 μm (Hansson 2000). A more recent development has been based on altering the surface chemistry of an implant in an effort to improve the osteogenic potential and create greater mechanical bone interlocking with the specific aim of more rapid integration. Hydrogen fluoride has been used to incorporate small amounts of fluoride into the crystal structure of the titanium dioxide. Such ion implantation into the superficial layer of a biomaterial may change the biological response to the implant. Future strategies are likely to attempt to increase osteoinductivity by making the metal surface carriers for biomolecules capable of controlling the early peri-implant response (Ellingsen *et al.* 2006).

14.1.4 Implant design

Implant design has usually referred to the design of the intra-osseous component. However, the design of the implant-abutment junction is also of great importance when it comes to prosthodontic management and long-term maintenance (Palmer *et al.* 2002). In general, implant reconstructions consist of an intra-osseous component sometimes referred to as a fixture. This is the component that is surgically placed into alveolar bone. The protruding surface of the fixture is designed with some form of locking configuration, which not only allows the engagement of a fixture mount to facilitate surgical implant insertion, but also allows for an abutment to be connected into the internal machining. In most situations, the abutment is attached to the implant by a screw mechanism thus creating a screw joint. The third part of the reconstruction is commonly referred to as the superstructure and this can be a single crown cemented over the abutment or in a multiple setting a coping that is secured by a further screw.

The design of a dental implant is based on many interrelated factors including the geometry of the fixture and the design characteristics of the implant–abutment connection so that there can not only be long-term stability of the implant–tissue interface but also of the implant–abutment interface. In general, developing an ‘optimal’ implant requires the integration of many factors; material, physical, chemical, biological and economic. In reality all these factors cannot be optimised in a given design, particularly when the envelope of construction, namely approximately 4 mm of biomaterial, is restricted.

To date, the clinician is confronted with over 100 root-form endosseous implants to select from, with a variety of diameters, lengths, surfaces, platforms, interfaces and body designs (Fig. 14.3). Categorisation of these can be made in a number of different ways. A logical analysis can be based on general characteristics based on length, diameter and screw thread geometry, implant body shape and the different characteristics of the varied implant–abutment connections (Binon 2000).

14.1.5 General characteristics of a screw thread implant

The design characteristics of a dental implant can have a bearing on both the biological response to fixture loading as well as on the biomechanical strength and integrity of the prosthodontic components and superstructure. A dental implant must be capable of supporting the superstructure, able to withstand occlusal loading and subsequently transfer this load to the supporting tissues in a way that maintains tissue viability. Of importance in this role are the screw thread geometry and implant length and diameter.



14.3 Types of threaded implants.

Alteration of these features can alter the total surface area available for osseointegration and subsequently stress distribution.

Thread geometry

Historical development of the fixture led to the incorporation of threads to the fixture design, based on the rationale that macroscopically they effected the transfer of forces to the supporting bone (Brånemark *et al.* 1977). These threads, sometimes known as macro-threads also have an important function in affording a newly installed implant primary stability through mechanical means. Altering aspects of thread geometry such as the pitch, depth or flare can change the nature of the force applied to the surrounding bone by altering the ratio of compressive and shear stresses. Three thread shapes are currently used, the standard V-shaped thread (Brånemark System, Nobel Biocare AB, Göteborg, Sweden) is similar to the buttress thread (Steri-Oss System, Nobel Biocare AB). Both of these have ten-fold greater shear component of force than the square thread (Maestro System, BioHorizons Inc., Birmingham, Alabama) (Misch 1999a). With early designs, the thread feature commonly stopped short of the crestal portion of the implant with the rationale that a smooth surface could be offered up to the soft tissues. An increasing number of implant systems are now producing dental implants with threads up to the coronal portion. An

early pioneer of this concept was Dr S. Hansson. His work in developing new design concepts was based on the understanding that the tissue response around an implant was intrinsically related to the biomechanical aspects of a fixture. Hansson went on to develop the concept of engineering an implant with microthreads in the coronal portion (Hansson 1997).

Implant diameter

The early work by Professor P.-I. Brånemark was based on a single implant concept, although differing lengths were used, with the implant diameter set at 3.75 mm. Further development of implant systems has led to the production of narrower and wider diameter implants that have specific indications for use. Implants with a narrower diameter (3–3.5 mm) have been indicated for use particularly in maxillary lateral incisor and mandibular incisor sites. On the other hand, wider-diameter implants (5 mm) have been indicated for use in posterior areas of the mouth as being suitable for molar tooth replacements.

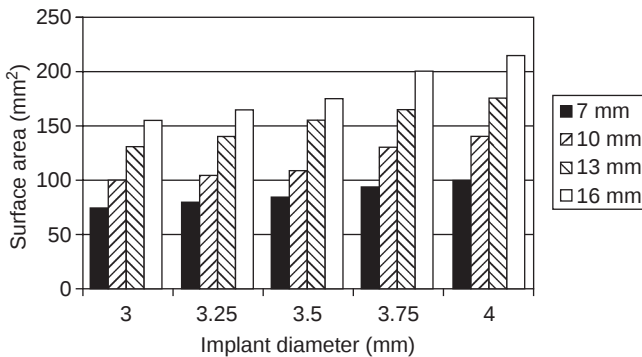
Changes in diameter can, however, affect fixture strength. Although a reduction of diameter by 0.25 mm can lead to, on average, a decrease in surface area of 5–8%, what is more important is the effect that reduction has on strength. Implant bodies are prone to fatigue fractures at the point of the apical extension of the abutment screw (Morgan *et al.* 1993) as the residual wall thickness of the fixture, taking into account the external thread depth and the internal screw thread, controls the resistance to fatigue fracture (Misch 1999a). This can increase the potential for fatigue fracture, especially in the presence of progressive crestal bone loss. The reduced loading platform can also have an effect on the overall strength of the prosthetic components (Binon 2000) as a reduced implant diameter ultimately affects dimension and hence the strength of the abutment screw (Fig. 14.4). The benefit of increased width has been shown in finite element analysis studies in that the greater diameter decreases the amount of stress at the crestal bone level (Matsushita *et al.* 1990). There is, however, the possibility that inadequate strain may be transmitted to the bone leading to resorption. There is no doubt that increasing the width of an implant has a bearing on the strength of the fixture, and also the strength of the prosthetic components secured within the fixture, while offering a greater surface area for osseointegration (Fig. 14.5).

Implant length

It has also been postulated that teeth with longer roots are better equipped to resist lateral loads, representing a better biomechanical system (Misch 1999b) with the supporting periodontal ligament capable of distributing



14.4 Comparison of screw dimensions. The reduced internal volume in narrow diameter implants leads to a reduction in space available for the abutment screw.



14.5 Effect of implant diameter on surface area.

forces to the alveolar bone along the whole length of the root. As a result, recommendations have been made that the longest implant should be chosen for the available bone and bi-cortical implant fixation has been advocated to achieve greater stability and anchorage (Brånemark *et al.* 1987).

This rationale has not been fully substantiated in long-term studies in the literature. One study has, however, shown that bi-cortical implants showed an implant fracture rate three times higher than mono-cortically

anchored implants with no appreciable improvement in success rates (Ivanoff *et al.* 2000). In addition, the stress transfer dynamics of osseointegrated implants, are somewhat different to those of teeth supported by a periodontal ligament. Photoelastic and finite element studies have shown that high stresses exist in the crestal bone around implants, both in function and in parafunction. It would appear from finite element analysis that 70% of stresses are concentrated in the crestal third of an implant regardless of implant length, and that changes in implant length have no effect in reducing the stress distribution around the crestal bone region (Misch 1999a). Applying principles relating to teeth, it would be logical to assume that an increase in implant length gives rise to a better crown/implant ratio. It has not, however, been shown that this principle relates to implants as it does to teeth. The stability of the structure and the stress distribution are more likely to relate to the stability of the abutment–implant interface and strength characteristics of this joint as opposed to implant length. The inter-relationship of width and length in the dimensions of an implant can have a role to play in situations where bone volume is compromised. The clinician has the ability to optimise the surface area available for osseointegration by altering the implant dimension. Such changes may, in some circumstances, have a negative impact on the strength characteristics of the prosthodontic restoration. Importance needs to be attached to the consideration of these factors, particularly in cases where narrower diameter implants are being considered, and the general implications considered would suggest that the width of an implant is more critical than its length.

14.2 Biomechanical response to loading

14.2.1 Transmission of loads

When a load is applied to a prosthesis supported by implants, two stages of load transmission are important for the successful performance of the entire design. The prosthodontic superstructure is primarily subjected to occlusal loading which has to be relayed to the implant. Secondly the load must be successfully distributed to the surrounding bone while maintaining its viability. The close apposition of bone to titanium allows for this successful stress distribution without any relative motion between the implant and the bone (Brånemark *et al.* 1987), although the acceptable load limit of bone under these circumstances is not fully known (Glantz *et al.* 1993). The nature and magnitude of forces generated will therefore have a bearing on the ability of the whole implant assembly to resist loads such that the superstructure, the implant or the bone are not stressed beyond their long-term fatigue capacity (Skalak 1983).

14.2.2 The mechanics of occlusal forces

Occlusal forces can be generated during mastication, deglutition, intercus-pation and in impact conditions. In addition, in some individuals, parafunctional habits can produce abnormally high loads during clenching or grinding. The amount of load applied during normal chewing can vary greatly. Dental factors that affect the degree of bite force generated include parafunction, position of tooth in the arch, masticatory dynamics, the nature of the opposing arch, direction of load forces and the crown/tooth ratio (Misch 1999b). As bite forces are three-dimensional, they can also be affected by the size and hardness of a bolus of food, cuspal inclination of the teeth and chewing motion (Weinberg and Kruger 1995). Variations in bite forces have also been reported, with factors such as occlusion, age, anatomy and ethnic, dietary, gender and health status making many of the results difficult to interpret (Brånemark *et al.* 1977).

Numerous studies have attempted to quantify the bite forces generated in human beings in edentulous, partially edentulous and dentate subjects, and, consequently, a wide range of values have been reported in the literature. The diversity of reporting has also been compounded by the different types of bite forces that can be recorded, including maximum bite, chewing and swallowing forces among others (Schnitman *et al.* 1988). Many different measuring techniques and devices have also been used, ranging from force transducers placed between the teeth and capable of evaluating forces parallel to the measuring axis, to strain gauges small enough to be placed in dental restorations which are capable of precise measurement (Osborn and Mao 1993). The latter can more readily be applied to dental implant studies as the nature of the restoration can allow for the gauges to be directly attached to the desired level of the implant stack (Brunski and Hipp 1984; Richter 1995). The net result of these factors would explain the wide variations in the reporting of bite forces within the various regions of the oral cavity (Table 14.1). A qualitative analysis of bite forces would allow certain assumptions in that the preferred chewing side is generally where the bite force is greatest, with occlusal forces generated in posterior sites being greater than in anterior sites. As would be expected, progression from a natural full dentition to removable dentures leads to a decrease in bite force and, conversely, functional improvement occurs when dentures are abandoned for osseointegrated bridges (Haraldson and Zarb 1988). Table 14.2 shows the effect that implant-retained restorations can have on the ability of the masticatory complex to increase bite and chewing forces when compared with the edentulous state.

What is of greater importance is the quantitative analysis of bite forces as this information is of more use in experimental and clinical bioengineering. Tremendous variation can be seen within the data and this can have a

Table 14.1 Maximum bite force

Reference	Age (years)	Number	Bite force (N)				Comments
			Incisor	Canine	Premolar	Molar	
Braun <i>et al.</i> (1995)	26–41	142				710	Between premolar and molar, male 789N, female 596N
van Eijden (1991)	31.1 ± 4.9	7		323–485	424–583	475–749	Second premolar and second molar, left and right. Converted figures
Dean <i>et al.</i> (1992)	Adult	57	150			450	Measured in left and right first molar
Bakke <i>et al.</i> (1990)	21–30	20				572	
	31–40	20				481	
	41–50	20				564	
	51–60	17				485	
	61–70	8				374	
Braun <i>et al.</i> (1996)	18–20					176	First molar or first premolar

Dentate or partially dentate subjects without dental implants; adapted from Misch, 1999a.

Table 14.2 Implant-related bite and chewing forces

Maxilla	Mandible	Total subjects	Maximum bite force (N)	Chewing force (N)
Nature	Natural	1059	295–660	95–258
Fixed bridge	Natural/fixed	36	320	100
Cantilever	Natural/fixed	24	264	50
Part denture	Part denture	24	199–214	NA
Full denture	Part denture	31	87–142	NA
Full denture	Implant bridge	14	44–253	NA
Full denture	Implant bridge	15	50–128	NA
Full denture	Cantilever	14	32	NA
Full denture	Full denture	399	18–196	17–153

NA, not analysed. Adapted from Schnitman *et al.* (1988).

direct effect on any study aimed at investigating the ability of a biomaterial to withstand oral forces. With regard to dental implants, many *in vitro* studies are based on the application of loads to investigate the mechanical endurance and failure mode of a particular component or fixture. One can therefore scientifically justify *in vitro* testing of dental implant structures across a wide and excessive range of loading values based on the wide variability of data reported in the dental literature.

14.2.3 Types of forces

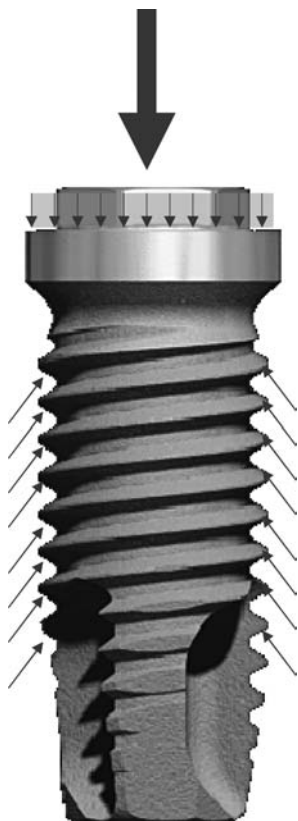
The forces that are generated are typically three-dimensional with components directed along one or more of the clinical co-ordinate axes. The effect of this is to resolve the force into a combination of components in any given plane, with the same magnitude of force having a different effect on the bone-implant interface depending on the direction in which it is applied. The main types of loading on the implant assembly that need to be considered are axial (compression/tension) forces and bending moments (Rangert *et al.* 1989; Quirynen *et al.* 1992).

Axial forces

Axial loads generate a greater proportion of compressive stress than tension or shear forces; this is of importance as both the implant structure and bone are more capable of handling compressive stresses than shear forces (Misch 1999b). A predominance of axial loading usually indicates a high load bearing capacity for the implant and supporting bone (Fig. 14.6) (Palacci *et al.* 1995).

Bending moments

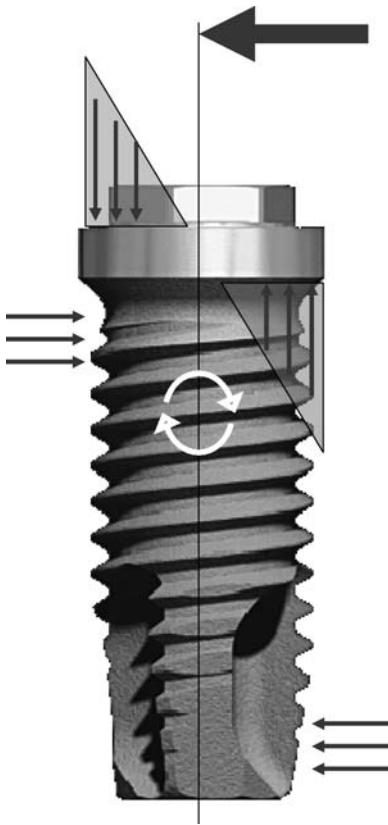
In both multiple- and single-unit restorations, bite forces create components of vertical loads and also transversal forces that give rise to bending moments on the crown-abutment-implant complex. Specific transverse bending loads can also be caused by premature contacts, bruxism or significantly angled implants (Misch 1999a). Bending movements can create high stress levels in implant components causing fatigue or component fracture. Adverse reactions at crestal bone levels surrounding the implant (Brunski 1988; Rieger *et al.* 1990a) can be caused by bending moments due to the higher concentration of stress gradients at the bone-implant interface (Fig. 14.7) when compared with true vertical loads (Rangert *et al.* 1989). High bending moments can exceed the mechanical load limits of the implants and are therefore more significant than axial forces (Glantz *et al.* 1993).



14.6 Axial load distribution. The morphology of the threads can have an influence on the nature of compressive force created within the bone around a machined implant (figure adapted from Palacci *et al.* 1995).

14.2.4 Prosthetic superstructure

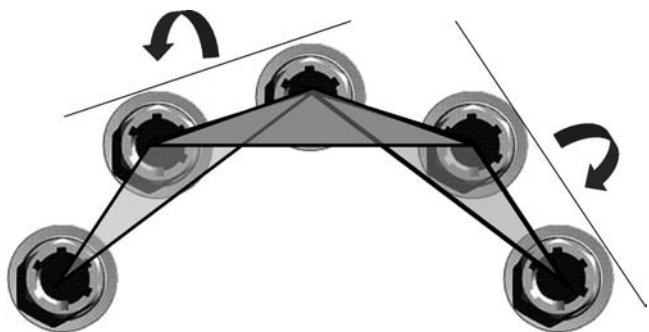
The nature of the prosthodontic rehabilitation has a direct influence on the type of loads transmitted to the implants. The full-arch restoration is based on the placement of multiple implants in a curved line which would appear to create an inherent capacity to counteract the transverse forces with axial forces. Any bending moments created around a line combining two implants is counteracted by the implants placed off the line experiencing axial forces (Fig. 14.8). The superstructure has the inherent feature of cross-arch stabilisation (Palacci *et al.* 1995). In a small, multiple-unit or single-tooth restoration, any force directed beyond the implant support can lead to bending moments. Even axial forces on these types of reconstruction can give rise



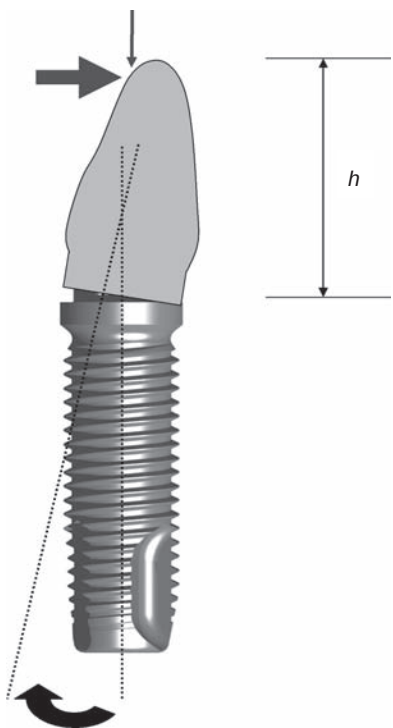
14.7 Transversal forces. Lateral forces challenge the body of the fixture as well as the crestal bone interface (figure adapted from Palacci *et al.* 1995).

to bending moments. Vertical load can be applied to an incisal or cusp tip offset from the implant resulting in the edge of the abutment acting as a fulcrum. The lever arm in this instance is the distance from the contact of occlusion to the junction between the abutment and fixture (Fig. 14.9). The effect of the bending moment is hence either directed to the bone–implant interface or at the abutment screw joint inducing high internal forces (Rangert *et al.* 1989). This situation can be more common in the single-implant molar restoration where the tooth crown dimension is much larger than the diameter of the fixture, leading to possible bending in all directions. Similarly the incisal tip of an anterior single-tooth restoration may be offset with regards to the implant body leading to high leverage forces.

The design of the implant system therefore has to be able to transfer the forces encountered at the most coronal aspect of the superstructure, through the intermediary prosthetic components to the bone supporting the implant,



14.8 Cross-arch stabilisation. Multiple-implant reconstructions can react to off-axial forces, with similar principles to those found in civil engineering (figure adapted from Palacci *et al.* 1995).



14.9 Bending moments on a single-tooth restoration. The effect of the bending moment is related to the length of the lever arm (h).

with little relative displacement of either the bone or the implant. Design features are also important as the successful dissipation of these forces is completely controlled by the geometry of the implant system and superstructure (Misch 1999b).

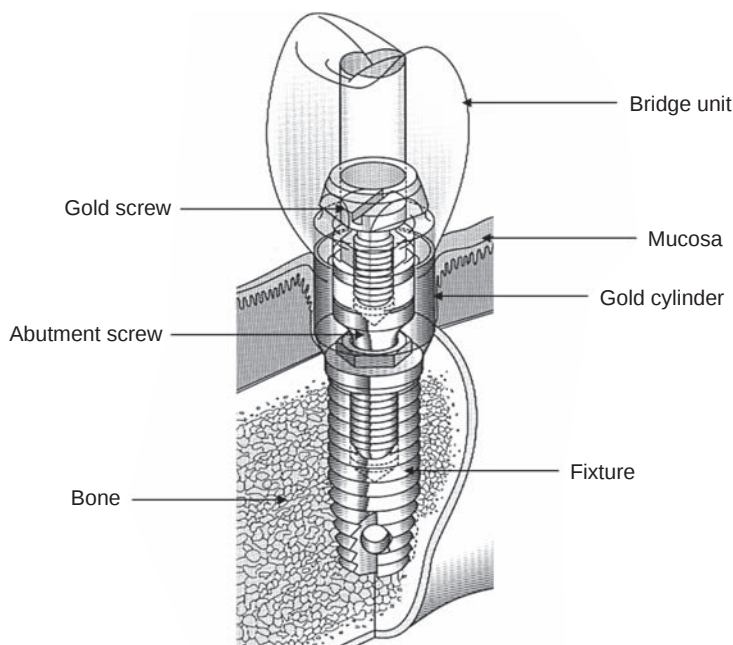
14.3 The implant–abutment connection

An important factor relating to the abutment–implant interface is the ability for it to transfer occlusal and other loads to the bone through the connection mechanism without a technical failure of the assembly. The geometry of this joint is one of the primary determinants of joint strength and stability (Binon 2000).

In the seminal work carried out by Brånemark *et al.* (1987), the connection mechanism was based on an external hexagon coupling mechanism. In its inception, this design primarily existed to permit engagement of a torque transfer coupling mount during surgical insertion, allowing the implant to be rotated into place. Subsequently the hexagon served as an indexing mechanism between the implant and the abutment component and with the growing application of dental implants in the single-tooth restoration, it also acted as an anti-rotational feature for the single crown. Long-term clinical data on the performance of the implant–abutment connection up to the mid 1990s were solely based on the external hexagon. This was mainly because most emerging implant systems at that time were clones of the Brånemark external hexagon design. From a performance perspective, however, the expanded utilisation of the hexagonal design resulted in a number of significant prosthetic and restorative complications. As a result many existing companies altered the specification of the hexagon while others adopted different engineering principles in the design of their implant–abutment connection. In 2000, there were some 20 different implant–abutment interface geometric variations available (Binon 2000). Although product improvement is commonly claimed by manufacturers of implant systems, little long-term data exists on many of these and the divide between optimisation and innovative marketing can remain somewhat blurred.

Notwithstanding the differences, in most systems, the implant–abutment connection is based on a screw-joint mechanism. An understanding of this mechanism, and the mechanical factors that are associated with it, is therefore important and the basic principles of screw joints can be illustrated using the external hexagonal connection.

The external hexagonal extension is used in mediating a butt joint with a matching internal hexagonal recess in the prosthetic abutment, creating a primary docking device (Binon 1995). The implant–abutment assembly is then secured with an abutment screw creating the classical engineering



14.10 Cross-section of an implant assembly.

screw joint. In multiple-unit prosthetic reconstructions, a secondary screw which is used to secure the superstructure to the abutment may further extend the screw-joint mechanism. Therefore, in screw-retained restorations, the implant anchorage unit consists of a fixture, the abutment and the tooth reconstruction, which are connected by the abutment screw and the gold screw respectively (Fig. 14.10).

14.3.1 Mechanical principles of a screw joint

The mechanical principles of a screw-joint assembly are based on the screw being tightened to a level where the component parts are clamped together such that the application of stresses to the joint do not result in its loosening. This is usually achieved by applying a known tightening force (torque) to the screw which causes it to elongate. The elongation of the screw, which should be within its elastic limit, induces a preload which produces a clamping force between the screw head and its seat, placing the components under tension and preventing their separation when subjected to external forces. Achieving optimal preload allows the joint to resist repeated loads from normal masticatory forces, which may introduce stress exceeding the fatigue life of the screw. It also prevents external forces from eroding the

preload, leading to a loosening of the joint (Rangert *et al.* 1989). Of importance is the fact that a screw joint will start to open when any externally applied force starts to exceed the joint strength of the assembly created by the preload. This leads to the process of screw loosening.

An apt description by Bickford of the process of screw loosening, which occurs in two stages, is provided by Burguete *et al.* (1994).

Initially external forces applied to the screw joint, for instance, during chewing, lead to the effective erosion of the preload in the screwed joint. The screw can be thought of as a spring, stretched by the preload, for which the stretch is maintained by the friction forces in the threads. Any transverse or axial external force that causes a small amount of slippage between the threads, no matter how small releases some of the stretch and some of the preload is lost. At this stage, the greater the joint preload, the greater will be the resistance to loosening, because the friction forces between the threads will be greater and a large external force is required to cause slippage. In the second stage of loosening, the preload is below the critical value so that the external forces and vibrations cause the mating threads to turn or 'back off'. Once this stage has been reached, the screwed joint ceases to perform the function for which it was intended and has failed.

The problem can be further compounded in a screw-retained restoration. Initially, the abutment screw secures the abutment to the implant head with the optimal preload applied. When the gold retaining screw is torqued into the superstructure, the compressive stress created by the preload on the gold retaining screw can reduce the preload at abutment screw level by as much as 50% (Sakaguchi and Borgersen 1995). *In vitro* testing has also shown that the weak link in such an assembly is the abutment screw and not the gold retaining screw (Basten *et al.* 1996).

14.3.2 Factors affecting screw loosening

Several factors can cause screw loosening and loss of preload. In addition, there are also factors that can increase the preload making a joint more resistant to breakdown.

Overload

Occlusal overload and excessive bending moments can create forces on an implant assembly that are larger than the yield strength of the screw, resulting in the plastic deformation of the screw. This results in a loss of preload in the screw stem and, consequently, loosening would occur. Similarly, overload can also occur if the implant position is not optimal. In such cases, offset loads can lead to excessive bending moments (Jorneus *et al.* 1992).

Torque applied to screws

Screw joints require the application of torque to achieve the necessary clamping. From a clinical point of view, specified torque values are recommended for both the abutment screw and the gold retaining screw for most implant systems. For a given screw joint, optimal preload and torque values can be determined on the basis of mechanical and material properties (Binon 1996a). The degree to which a screw is tightened in relation to its properties will determine the preload. It is important to select an appropriate level of tightness based on the fatigue life of the screw and the optimum preload of 75% of a screw's yield strength has been recommended allowing the screw to function within its elastic range (Haack *et al.* 1995). Over-tightening a screw beyond its yield strength can drastically decrease the fatigue performance of a screw (Burguete *et al.* 1994).

Physical properties of the screw

One of the most critical aspects is the ability for small screws within the implant complex to hold the various components together. Manufacturers have, over a period of time, altered screw designs to improve the stability of the implant–abutment connection. The emphasis has been on lowering the loss of input torque to friction, allowing a higher preload to develop. Changes have included an increase in screw stem length together with a shortening of thread lengths. Changes have been made to the material of the screw, as this is seen as one of the most significant factors determining bolting characteristics. Titanium screws within a titanium implant can result in 'galling', a form of adhesive wear that occurs during sliding contact; this together with the frictional resistance can limit the preload characteristics (Binon 2000). In contrast, a gold alloy abutment screw has been shown to have three times the yield strength of a titanium screw of the same dimensions, allowing a higher torque application with better maintenance of preload. It is possible to produce a higher preload by lowering the effect that friction can have on the input torque. Changes such as shortening the thread lengths and applying dry lubricant coatings can help to reduce the frictional resistance encountered during screw tightening. By applying dry lubricant coatings such as pure gold to a gold–palladium abutment screw, the preload can on average be increased by 25% for a given torque when compared with identical non-coated screws (Porter and Robb 1998). The design of the head of the screw is also of significance. A conical shape to the screw head can lead to the loss of a major part of the torque due to increased friction between it and the abutment (Jorneus *et al.* 1992). From a practical viewpoint, components are often passed from surgery to laboratory during the various trial and construction stages. The condition and age

of the screw may have a bearing on the preload attained, it would seem prudent to differentiate between laboratory screws and definitive restoration screws.

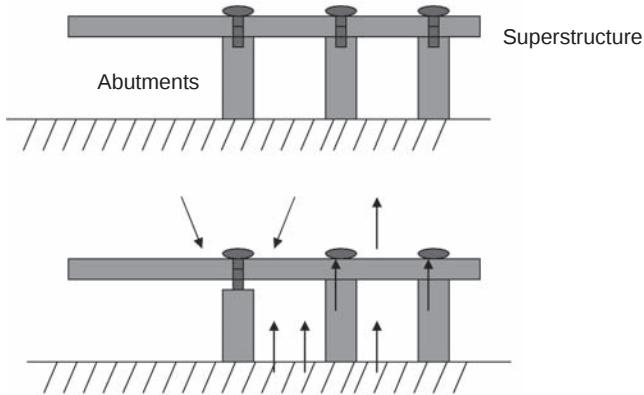
Component fit

A major proportion of components are machined and there can be a significant variation with regards to the external hexagon assembly in the quality of fit and the degree of rotational freedom between abutments and implant head (Binon 1995). This problem can be compounded when, in the presence of clone abutment-implant connections, components are used from different manufacturers. With regards to the external hexagon, the degree of rotational freedom can be doubled from approximately 5° to as high as 10° when components are paired from different manufacturers. It is interesting to note that rotational misfit of more than 5° can give rise to a 63% reduction in the number of cycles to loosening (Binon 1996b).

Other factors, such as debris and the presence of asperities from the machining process, can lead to embedment relaxation of mating thread and component surfaces leading to a loss of up to 10% of preload. Micromovement when external loads are applied can also lead to wear of irregularities, leading to settling with loss of preload (Jorneus *et al.* 1992).

Framework misfits

Another aspect of component fit becomes more pertinent with multiple units. In a full-fixed-arch reconstruction, the implant superstructure is the part of the prosthesis that is attached to the implants. It usually consists of cast metalwork onto which prosthetic teeth are constructed. Within such a casting, all of the mating sections should meet accurately, intimately and simultaneously allowing for a passive fit. Stresses created by ill-fitting superstructures can result in screw loosening and implant overload (Lang *et al.* 1999). Theoretical calculations have shown that the safe life expectancy of a gold retaining screw is approximately 12 years based on sound construction and loading. This figure can be reduced to an order of weeks if the quality of fit is compromised (Patterson and Johns 1992). The level of acceptable fit still remains to be defined, with clinical judgement underlying the subjective nature of evaluation. Discrepancies of fit ranging from 30 to $150\mu\text{m}$ have been suggested as acceptable (Klineberg and Murray 1985). Investigations for framework fit can be carried out using the photo elastic method. Under such scrutiny, fit discrepancies as small as $6\mu\text{m}$ can induce stress on a cast superstructure with the area of maximum stress found among the intermediate abutments regardless of where the



14.11 Superstructure misfit. Top panel, a passive fit results in simultaneous contact between all aspects of the superstructure and the abutments allowing the preload to be optimised within the retaining screws. Bottom panel, a misfit creates undesirable stress within the retaining screws, superstructure, abutments and surrounding bone.

discrepancy was noted (Millington and Leung 1995). Fig. 14.11 shows the effect that a misfit can have on stress distribution. For illustration purposes the exaggerated misfit has been represented by altering the abutment height. In reality the superstructure would show a deformation. The dimension of a framework is largely determined by anatomical constraints and is also dependent on the number and distribution of the implants. Both the design of the prosthesis, and the number and position of the supporting implants, have a significant influence on stresses in bone and within the components of the assembly. Where implant placement is not a feasible option in posterior sections of the jaws through the lack of bone height, it may become necessary to add cantilever sections to the framework. The length of such extensions, which can be in the range of 10–20 mm, with the longer length better tolerated in the mandible, having further bearing on stress distribution.

Based on the above discussion, in any screw joint, the conditions that need to be met to accomplish the desired function should ensure that optimal preload is achieved with recommended tightening torques to maximise the fatigue life of the assembly. Precise fit between the components of the implant assembly should exist and the external forces placed on the assembly should be within the yield strength of the screw.

14.4 Mechanical complications

The early development of the osseointegrated technique was based on the use of multiple implants, framework and gold retaining screws for the rehabilitation of the completely edentulous arch. In these early stages, technical complications mainly related to loosening screws and implant fracture (Brånemark *et al.* 1977). Further problems related to mechanical failure can also occur within other aspects of a dental implant assembly, particularly when the single-implant restoration is concerned. The nature, direction and magnitude of loads on the single-tooth implant are considerably different from multi-unit restorations. Different component combinations need to be used to be able to cope with this. As a result, the nature and presentation of complications can differ (Jemt *et al.* 1989; Adell *et al.* 1990; Naert *et al.* 1992b; Babbush and Shimura 1993; Polizzi *et al.* 1999).

14.4.1 Screws: loosening and fractures

A common problem associated with osseointegrated implants is loosening of either the gold retaining screw that attaches the superstructure to the abutments or the abutment screw itself.

Gold retaining screws

The gold retaining screw historically has been seen as the weakest link in the implant assembly. The aim of having built-in safety and hence retrievability was based on the principle of protecting the bone–implant interface from overloading (Zarb and Schmitt 1990). The stability of the retaining screw can be dependent on the nature of the prosthetic design and the variability of biting forces (Haack *et al.* 1995). Improperly fitting frameworks can also place undue stresses on the screw and so affect its performance. The configuration of implant position in relation to mechanical loading can also have an effect. If any of these factors compound with parafunctional behaviour then the risk of screw fracture can also exist (Zarb and Schmitt 1990). Gold screws can also be more prone to loosening in reconstructions within the maxilla compared with the mandible based on the anatomical differences between the two jaws together with issues of configuration (Jemt *et al.* 1992).

Abutment screws

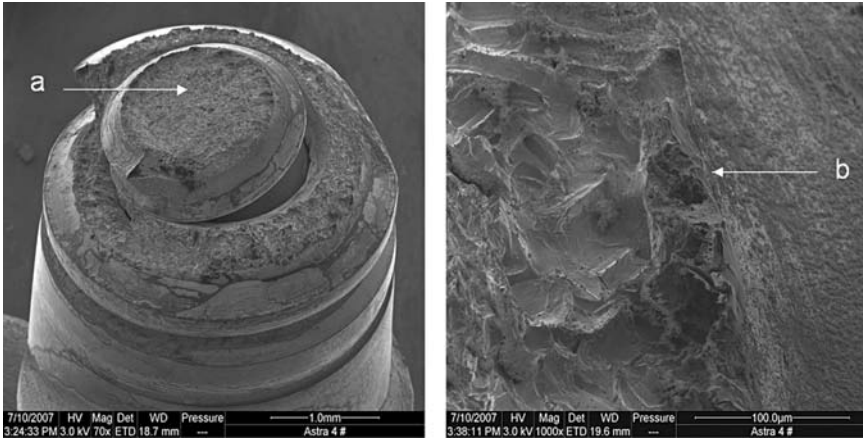
Abutment screw loosening and fractures can also occur. The evolution of osseointegrated techniques for single units and cemented restorations has meant that the screw joint must function differently. It has to maintain the

integrity of the abutment–fixture complex without loosening or fracture due to its inaccessibility. In essence, this means that the screw joint can no longer function as the safety or retrievable feature, particularly in the single-tooth restoration. The material specification of the screw can have an influence on stability. Gold abutment screws can show greater stability compared with titanium screws in some implant–abutment connections. The predominant complication in one single-tooth study involved loose abutment screws that occurred in 43% of restorations. Loosening occurred once in 30% and twice or more in 13% of the restorations completed. Retrievable titanium abutment screws were replaced with gold ones without further complications (Ekfeldt *et al.* 1994).

An important factor in maintaining screw stability is the application of the correct torque to ensure that the optimal preload has been achieved. Historically, many of the screws have been tightened purely by hand, and operator variability and design of the screwdriver handle can have a dramatic effect on this. When asked to produce a specific torque, clinicians showed variances between 0.71–13.1 for the 10 Ncm test; 1.4–33.7 for the 20 Ncm test; and 8.2–36.2 for the 30 Ncm test (Burguete *et al.* 1994). Specified torque application using either manual or mechanical torque wrenches has helped to considerably reduce the frequency of screw loosening (Jorneus *et al.* 1992; Haas *et al.* 2002). The design of the implant–abutment connection has a considerable influence on the vulnerability of the abutment screw to loosening, and this will be discussed later in this chapter. An important aspect of increasing screw stability is that the fixture strength has to match the screw-joint strength in situations of high lateral bending forces (Dixon *et al.* 1995).

14.4.2 Implant fractures

Although fracture of the fixture component of an implant assembly can be a rare occurrence, the clinical consequences of such an event can have a significant impact on the patient (Morgan *et al.* 1993). Many factors can be implicated in the aetiology of implant fractures. The design and material of the implant system, non-passivity of the framework, and physiological or biomechanical overload can be critical factors for fixture fracture (Balshi 1996; Lang *et al.* 1999). Implant fractures can occur due to overload or fatigue. Comparing the characteristics of the fracture surface can enable a differentiation between the two. It has been reported that fixtures that fracture in clinical use appear to do so by fatigue. In one study, clinically fractured implants were removed and the crack characteristics compared with implants subjected to fatigue and overload bench tests (Fig. 14.12). Experimentally induced overload fractures together with clinical screw fractures were observed using scanning electron microscopy (SEM). It



14.12 Scanning electron microscopy view of a fixture fracture following catastrophic dynamic testing. *a* Deflection and fracture of the abutment screw is evident. *b* The fracture zone is differentiated under higher magnification.

was found that the clinical patterns of failure were similar to those produced by *in vitro* fatigue loading and not those of overload (Morgan *et al.* 1993). An implant that is fully embedded in bone has protection from distortion by adverse bending stresses from the bony housing. If crestal bone loss occurs around the neck of an implant, then the exposure of the implant to higher local stresses can give rise to fatigue-based crack initiation and propagation. The critical amount of bone loss would appear to be to a level that corresponds to the end of the abutment screw. At this level, the cross-sectional area of the implant changes from a solid composite cylinder to an annulus with a corresponding area of internal weakness. This coupled with a sudden change in external geometric configuration, such as a sharp corner at the root of a thread, may precipitate failure (Morgan *et al.* 1993).

Although the design of an implant system can be implicated in the likelihood of fracture, no data currently exist to substantiate this statement. It is possible that parafunctional overload (Balshi 1996) in the presence of critical crestal bone loss are the overriding factors leading to implant fracture.

14.5 Design variations within dental implant systems

As the types of applications for dental implants increased, so did reports of technical complications associated with the external hexagonal platform. These problems have been mitigated by the overall connection undergoing a number of modifications. In some systems the height of the hexagon has been raised from 0.7mm up to 1.2mm to offer greater

lateral resistance. The flat platform width has also been altered to offer more resistance against bending moments. The abutment screw has undergone changes of material, length of the shank, thread design and coating to improve preload characteristics. Various companies, in order to overcome the intrinsic deficiencies of the hexagonal connection, have introduced entirely new implant–abutment connections with considerable changes in design and coupling mechanisms. As the geometry of the connection is one of the primary determinants of joint strength, changes in design and type can affect the performance and stability of the dental implant assembly.

The sheer variety of different implants on the market can make categorisation difficult. For a simplified approach it would make sense to make a distinction between two surgical concepts that affect implant design and focus on the implant–abutment connection as a differentiating factor. The general shape and features of an implant can be based on the surgical approach used to place the implant. The traditional development by the Brånemark team is based on a two-stage surgical approach. The fixture component is inserted into the alveolar bone and the soft tissues are closed to allow for a suitable healing period. A second surgical procedure is then undertaken to expose the fixture into the oral cavity and to place a healing abutment which projects through the mucosa. The purpose of this trans-mucosal element is to allow the establishment of a mucosal cuff through which a direct connection for the superstructure can be made at the restorative stage. The fixture design therefore has to allow for it to be positioned flush with the alveolar bone. In contrast, the approach developed by the Schroöder team is based on advancing the development of the trans-mucosal screws originally designed by Ledermann. The surgical approach to this concept is based on a one-stage surgical technique with the neck of the fixture component left exposed into the oral cavity at insertion surgery. This procedure obviates the need for second-stage exposure surgery as the inserted fixture has an attached extension that extends it from the alveolar bone and through the mucosa. Although it is not the remit of this chapter to discuss the concepts described, it suffices to say that both methods are accepted procedures from a surgical point of view, although debate exists between the supporters of each method as to the validity of the other. What is obvious when both generic designs are scrutinised is that the biomechanical forces that the fixture is subjected to are going to be different in each case due to the presence of an extension on one of the designs. This will be discussed later.

Currently there are some 20 different implant–abutment interface geometric variations available. Implant–abutment connections are generally described as internal or external. The external joint has a flat platform with

the hexagon extending above the bearing surface resulting in a butt joint between the implant and the abutment. The internal connection is generally based on having a deep internal chamber with an anti-rotation and indexing feature. The development of these connections has been based on the theoretical assumption that the screw is protected from loads or subjected to lower loads as the connector provides a more intimate contact with the implant walls, thereby resisting micromovement. The ability to engage an internal space within the implant has also allowed for abutment connections at varying depths and configurations depending on system design. Internal connections, as a result, display a variety of mating configurations, including the butt joint, internal or external bevels and the internal cone connection.

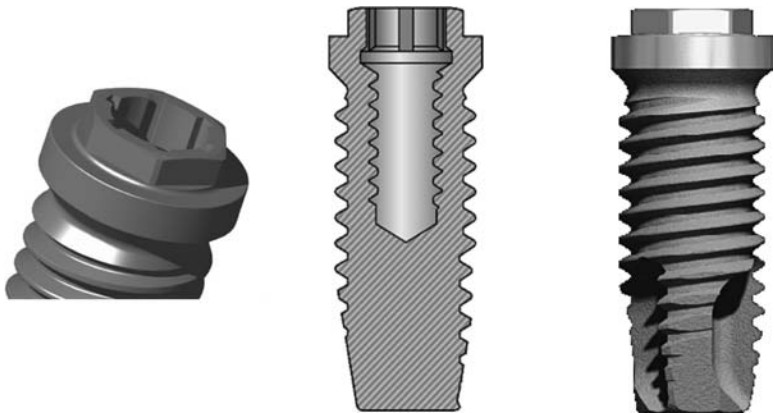
The internal butt joint can be based on an internal hexagonal feature or use lateral cam engagements to provide seating and indexing. The deeper cylindrical joint can offer improved resistance to lateral loads with a resistance to micromovement and consequently joint opening (Mollersten *et al.* 1997). In some systems the internal cylinder can engage the internal walls of the implant with reports that this design makes the implant 60% stronger than the external hexagonal connection (Hutmacher *et al.* 1998). The internal bevel connection is based on internally sloping the flat platform of the butt joint on the implant and having the male hexagon extending from the abutment. The design has effectively reduced the vertical height of the platform and made seating components easier. However, in narrower diameter implants, this can lead to thin implant walls at a critical level, which in combination with overload can result in wall fracture (De Bruyn *et al.* 1999). This has led to a design modification introducing a horizontal shelf immediately below the lead-in bevel along with an increased wall thickness, thereby improving strength and fatigue resistance. The rationale of the internal cone connection is that it yields a mechanically sound, stable and self-locking interface. The connection has been based on a form of Morse taper, although in general the mating angle between the components is around 8–11° depending on the system. Almost all of the connections featured in implant systems are based on a screw retention design with either single components incorporating the configuration of the connection and the screw or two-piece components where the screw is separate. One novel design has eliminated the screw altogether by introducing a true Morse taper of 1–2°. The tapered post is designed to fit inside a smooth-mirror image shaft within the implant. Insertion is by means of a sharp blow on the long axis of the implant. Removal is based on a twist and turn manoeuvre using forceps. Although this type of connection has demonstrated stability in function, it has been claimed that it lacks flexibility from a restorative perspective (Binon 2000).

14.6 Overview of dental implant systems

A comprehensive review of dental implant systems cannot be possible within the context of this chapter as there are approximately 100 root-form implant systems available worldwide from different manufacturers. There are many design variations on the generic types of implant–abutment connections together with different implant shapes, thread specifications and surfaces. Implant system manufacturers have a tendency to highlight variations as being superior to their competitors and also suggest that the integrated relationship of all the design features creates a functional complex essential for long-term success. The following discussion is not meant to be exhaustive but aims to illustrate different implant system types by highlighting the collective features of some of the commonly used variations.

14.6.1 The Brånemark implant system

The Brånemark implant system consists of parallel-sided, threaded root-form fixtures, which are solid screws of differing diameters. The implant–abutment connection is based on the external hexagon and has a flat top, which offers a butt joint (Fig. 14.13). These implants originally had a machined surface, which under high magnification exhibited surface irregularities and ridges. The type of surface was considered to be optimal as smoother surfaces failed to integrate and rougher surfaces were thought to be more prone to corrosion. With developments in surface technology the current system has an oxidised surface known as TiUnite. More recently, different thread forms have been introduced to enlarge the product portfolio.



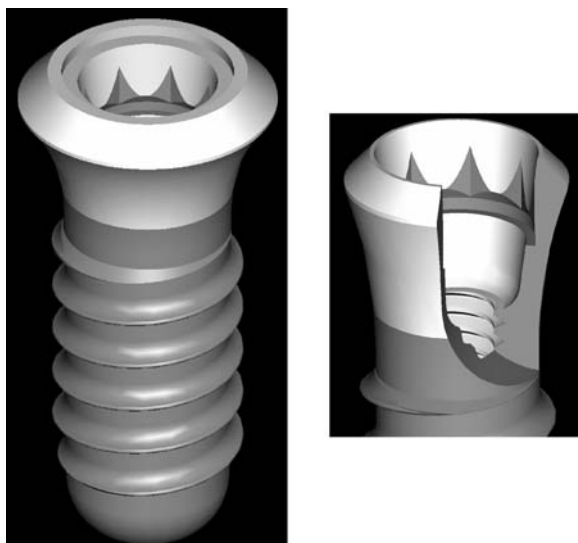
14.13 The Brånemark implant system.

14.6.2 The Straumann implant system

The Straumann implant system was originally developed by Professor André Schroöder in Switzerland and differs from many other implant systems in that it has a one-stage surgical protocol. This surgical concept has led to a design incorporation of a polished trans-mucosal collar, which allows the implant to be inserted into bone and maintain exposure within the mouth. The implant–abutment connection is based on the Morse taper and it sits, in view of the trans-mucosal collar, above the level of the alveolar bone (Fig. 14.14). In order to satisfy all aesthetic factors the trans-mucosal collar is available in two different heights allowing the vertical position of the fixture to be altered at time of placement. Traditionally, the system was composed of solid and hollow screws as well as hollow cylinders. The hollow designs were reported to greatly increase the surface available for osseointegration but have since been withdrawn. All current Straumann implants are a solid screw with a coarse thread pitch and with a sand-blasted, acid-etched surface. A current modification to the surface has been to increase its hydrophilic nature by introducing protective gas conditions during the manufacturing process and storing the implant in liquid conditions.

14.6.3 The AstraTech implant system

The AstraTech implant system consists of parallel-sided, self-tapping solid screws and a specific single-tooth implant which has a conical collar.

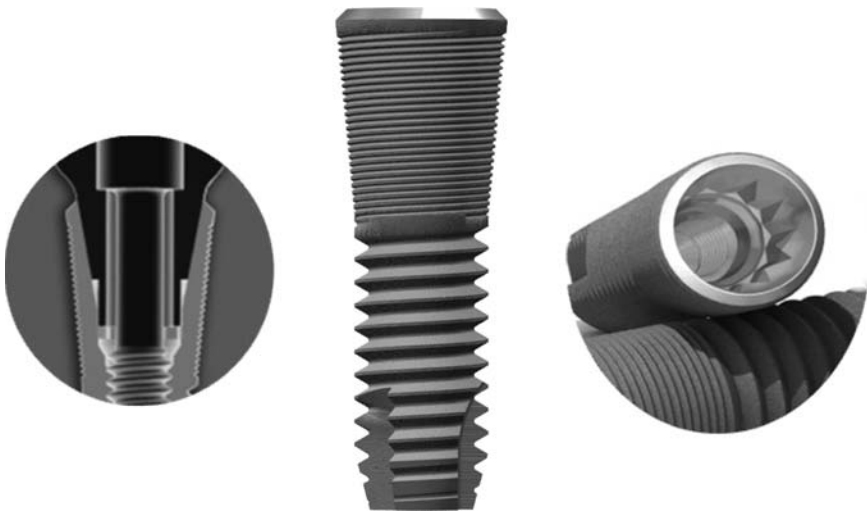


14.14 The Straumann implant system.

designs the implant–abutment connection is a conical one based on an 11° taper. The implant system is based on a two-stage surgical procedure and the coronal portion of this system is characterised by a zone of microthreads that are claimed to distribute stress more favourably at the marginal bone level. The implants have a roughened surface produced by grit blasting with titanium oxide. The current surface, termed Osseospeed, has surface chemistry modification by the application of a weak solution of hydrofluoric acid. This treatment claims to give a faster bone response resulting in a shorter healing time. Many reports for this system have shown that these implants do not show the degree of apical bone migration demonstrated by other, and in particular the butt joint, systems. It has been postulated that the combination of the features above lead to a stability around the implant–abutment junction facilitating a stable junctional epithelium within the periodontium (Fig. 14.15).

14.6.4 The Osteocare implant system

The Osteocare system is characterised by the presence of an internal hexagonal connection based on a bevelled platform. This design is also incorporated within the Zimmer Dental Implant System. Like most internal connections, the internal hexagon offers a more precise seating of the abutment than the external hexagon with a lower risk of component mismatch. In common with the internal cone connections, the internal hexagon offers a reduced vertical height for restorative components and the ability to dis-



14.15 The AstraTech implant system.

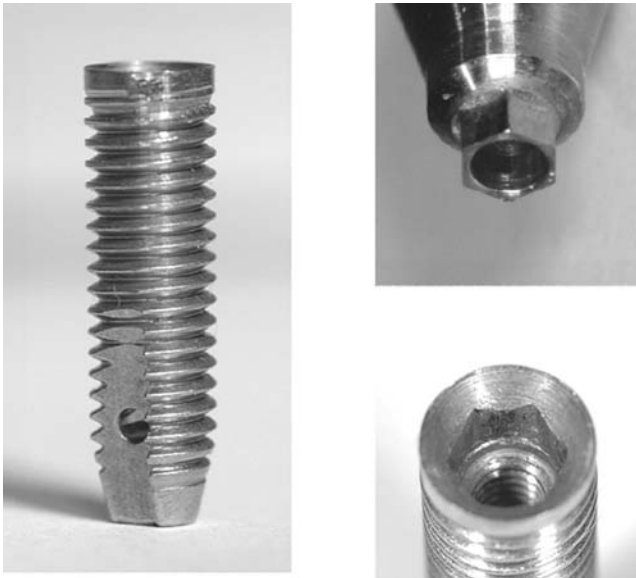
tribute lateral loading within the implant offers some degree of protection to the screw (Fig. 14.16).

14.6.5 The Replace implant system

The Replace system presents with an internal butt-joint connection with the anti-rotation element defined by the presence of three lateral cam engagements. The system has been designed in response to the problems associated with the external hexagon and shares the same surface and screw thread configurations as the current Brånemark implants. The internal connection again facilitates the clinical process although the flat platform has the potential for micromovement and the presence of a microgap (Fig. 14.17).

14.6.6 The Bicon implant system

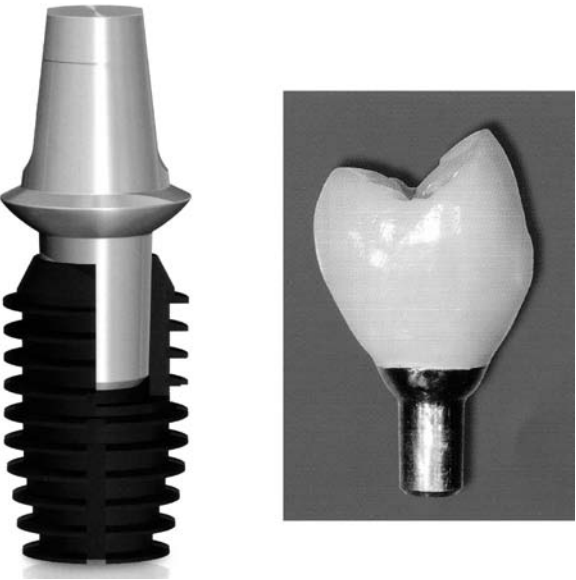
The Bicon system appears to be the only one available without a screw-retained abutment connection. It also lacks an anti-rotational feature. A 1.5° locking taper frictionally holds the components together. The implants themselves have fin or plateau root form designs allowing for shorter implant placement. The superstructures are tapped into place without using cement retention and it is claimed that this tapering lock offers a superior seal against bacteria thereby eliminating the microgap (Fig. 14.18).



14.16 The Osteocare implant system.



14.17 The Replace implant system.



14.18 The Bicon implant system.

14.7 Testing dental implant assemblies

Ideally, implants should not fracture, yield, fatigue, wear or otherwise degrade during *in vivo* use. To achieve the long-term success of surgical and prosthetic integrity for an implant-retained restoration it is important to investigate the effect of *in vivo* forces, load transmission at the various interfaces and the interfacial tissue response. Mechanical testing, numerical simulation and stress analyses are important methods that can be used in an effort to prevent failures, such that new materials and components can be observed before controlled clinical testing (Brunski 1988).

It is generally accepted that the majority of implant designs can transmit occlusal forces to the supporting tissues quite successfully without systematic failure (Natali 2003). What is of interest, however, is the fact that early implants were not designed with engineering principles in mind. A lack of knowledge on implant loading, bone-implant contact area and bone properties to mention a few, meant that design objectives could not be set before product development. This has been addressed in part by using the finite element method, although many of the parameters required for such analyses are still unknown.

The mechanical reliability of dental implants depends on a determination of the loading acting on the implant and how this is transmitted to the peri-implant bone through the implant itself. Occlusal forces create a complex configuration of loading which induce a consequent distribution of stress in both the implant components and the surrounding bone. In testing dental implant assemblies it becomes important that all the components involved are investigated, not only to allow for a greater understanding of the characteristics of the assembly but also to identify weaknesses within the design or the material. It has to be remembered that the type of loading, superstructure configuration, nature of the implant-abutment connection, shape and dimension of the implant, the implant surface and the properties of surrounding bone affect the load-bearing capacity of the whole system.

It has been suggested that the aim of mechanical testing should be to replicate wherever possible the conditions relating to mechanical and biological failure using models representing the clinical situation. The problem that exists is whether or not *in vitro* models and test conditions can accurately relate to the *in vivo* condition as described above. This problem also exists within stress analyses investigations. Evaluating the load transmission from an implant to the surrounding tissues in an effort to understand biological failure using techniques such as the finite element method and photoelasticity also has limitations. Nonetheless, engineering methods, both experimental and numerical, can make a significant contribution by simulating and characterising the critical conditions that an implant system can experience.

14.7.1 Mechanical testing

An important aspect of failure is time. In general, short-term failure and acute overload conditions can be fairly rare and are usually attributed to trauma or material and design flaws. The majority of mechanical failures can be attributed to catastrophic failure of an implant component from cyclic stresses over a period of several years. Mechanical testing can broadly be classified as static or dynamic. In a dynamic loading situation, loads are repeatedly applied at pre-determined stress amplitudes until failure occurs as a result of fatigue. Static tests such as compression bending, three-point bending and torsion tests are performed using test machines that slowly increase the load until failure occurs. Screw-joint mechanisms can also be investigated by characterising the behaviour of a screw in response to tightening and loosening. Conventional material testing can often be based on a single material, section or a sample of it. With dental implant systems, similar tests can be carried on individual components or on the whole assembly.

14.7.2 Torsional tests

Torsional loading tests can be utilised to test for maximum anti-rotational stability. Applying this test to an external hexagonal system has shown that torsional forces are capable of causing damage to either the mating surface of the abutment or to the anti-rotational element of the implant (Balfour and O'Brien 1995). There is a questionable validity in using torsional tests for dental implant assemblies. In systems with an anti-rotation feature, the common values for breakdown or deformation are likely to far exceed any forces generated within the mouth – by occlusal forces, hand instruments or calibrated torque wrenches. Torsional tests would, however, appear to be valuable investigations in abutment–implant designs with internal connections based on cone screw connections (Arvidson *et al.* 1992; Sutter 1993) which do not rely on positive indexing and are capable of rotation. Measuring the torque values and the degree of relative movement between the implant and the abutment would allow for an analysis of the degree of stability offered by the connection in the absence of any anti-rotational feature (Ubhi 2000).

14.7.3 Three-point bending tests

The three-point method of testing has also been applied to the implant–abutment assembly, as it is an appropriate method of testing the strength of a material or joint from an engineering perspective. The assembled samples in this test are subjected to a force perpendicular to the unit axis across

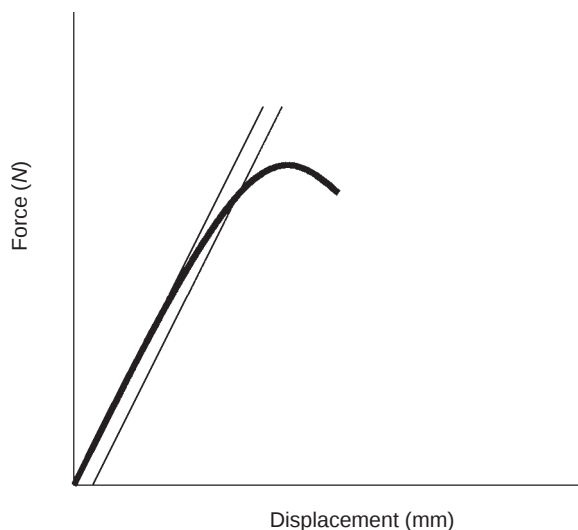
the interface to be tested. The test can be of value when comparing different types of joint configurations as it allows a relative comparison of bending moments and also a visual realisation of the deformation that has occurred. With dental implants, the test can have relevance when analysing the implant–abutment connection or the superstructure–abutment junction (Norton 1997).

14.7.4 Rotational movement tests

Rotational movement tests can be used in evaluating the degree of misfit between components and the effect that this has on screw-joint stability (Balfour and O'Brien 1995; Binon 1995). It has been claimed that as external loads always amplify dynamic changes in screw joints, any misfits and pre-existing deformation within the component stack will further enhance screw loosening (Binon 1996a). This test is likely to have more importance in comparative assessments of clone components in order to quantify the machining tolerances of manufacture.

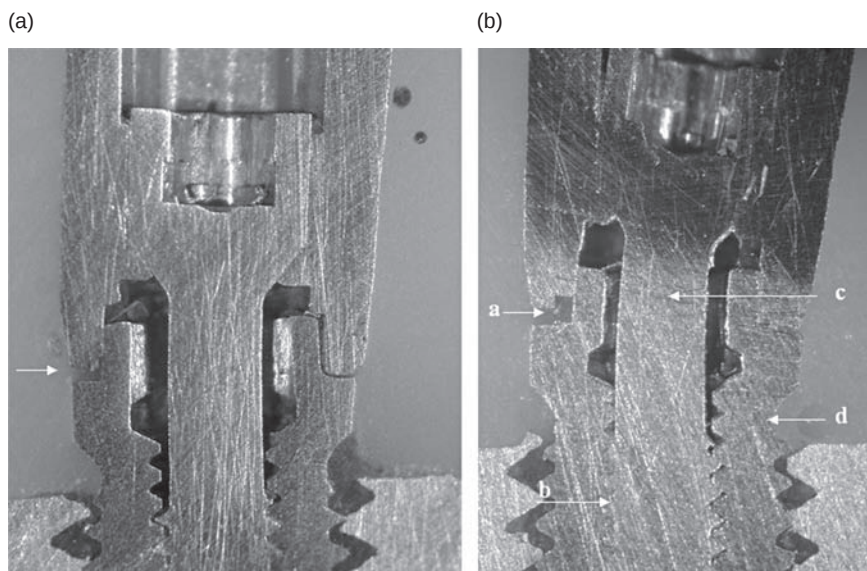
14.7.5 Compressive bending tests

Compressive bending tests can provide valuable information on the characteristics of a screw-joint assembly when subjected to static conditions. Resistance to bending forces in an implant system is essential for long-term success. In engineering terms, the strength of a material is defined by its ability to resist applied forces without yielding or fracturing. The rationale behind the compressive bending test is that it allows the application of ultimate failure loads in a manner similar to clinical cantilevers or severe single-tooth bending moments (McGlumphy *et al.* 1992; Balfour and O'Brien 1995). Although such severe conditions are unlikely to be encountered in the oral environment, the components under test can be analysed for the effects of this nature of loading. The tests can also be of use when comparing different implant systems (Mollersten *et al.* 1997), or in evaluating different parameters such as changes in component specification. Analysis can be based on the maximum force to total failure, although the nature of the test means that any implant assembly subjected to an attenuated force will deform. Characterising or quantifying gross distortion or failure can be considered meaningless, as these events tend to occur at loads beyond those generated within the mouth. The author's preference is to evaluate resistance to bending by using data based on the elastic limit of the assembly (Suleiman 2000). This can allow for analysis at a more relevant critical point of failure and can also allow for comparative evaluations (Fig. 14.19). In an effort to standardise with other testing standards, testing should be carried out at an angulation of 30° (Balfour and O'Brien 1995; Binon 1996a, 1996b;



14.19 Analysis method for compressive bending tests. The method is based on the concept of proof stress with values determined by the intersection of a line parallel to that of the proportional limit of the test. The standardised lateral shift in measurement allows for interpretation of test results that may not show a specific yield point.

Boggan *et al.* 1999). Altering the degree of angulation would have a bearing on the results obtained. Testing at a 90° angulation (McGlumphy *et al.* 1992; Mollersten *et al.* 1997) can represent a ‘worst-case’ approach although it may have little or no relevance to clinical situations. Calculations have shown that the failure mechanism for an implant system with a joint will be the same at all loading angles between approximately 6° and 90°. This has been explained on the basis that 0° loading gives rise to purely compressive loads which would not result in failure but that as the angle increases, a ‘critical’ angle is reached above which tensile loads occur and failure can be expected. The premise is that the failure mechanism would be the same but the magnitude of failure forces would differ according to the angle of testing (Mollersten *et al.* 1997). Cross-sectional analysis of progressive compressive bending tests can also help characterise the nature of deformation encountered within the implant–abutment complex. Figure 14.20 illustrates the changes that can occur within the implant–abutment connection. Loading initially challenges the preload within the abutment screw with a microgap at the junction of the connection (Fig. 14.20a). Further loading (Fig. 14.20b) increases the microgap (a) and creates compression within the ipsilateral aspect of the abutment screw threads (b), deformation of the shank of the abutment screw (c) and flexure of the body of the fixture (d).



14.20 Cross-section of test assemblies subjected to compressive bending. *a* joint opening, *b* abutment screw threads under compression, *c* distortion of the shank of the abutment screw, *d* distortion of the neck of the fixture.

14.7.6 Cyclic load tests

Cyclic loading tests can give valuable information on the dynamic failure characteristics of an implant assembly. Dynamic testing is commonly associated with fatigue, a mode of fracture whereby a structure eventually fails after being repeatedly subjected to a number of external dynamic load applications (Dally and Riley 1991). Failure occurs by the development of microscopic cracks in areas of stress concentration. Continuous loading leads to an insidious weakening of the structure leading to catastrophic failure resulting from a final loading cycle that exceeds the mechanical capacity of the structure. As such, the progression of fatigue failure is classified in terms of crack initiation and propagation leading ultimately to complete fracture and catastrophic failure (Suresh 1998). Dynamic loading tests on implants related to fracture mechanics are relevant in that reports of time-related fixture fractures in the clinical environment indicate that the fractures are fatigue induced (Morgan *et al.* 1993), although in many cases failure of the assembled components is possibly of greater importance. With an implant assembly, other events, equally time-related, such as screw loosening or fracture, may occur that signify failure of the restoration although visible cracks or fractures may not be present. Failure in such assemblies can therefore be defined as material yielding, deformation or

fracture and it becomes important to identify the critical failure point and the location of failure initiation.

With an implant assembly, although fatigue analysis is of importance in understanding fracture mechanics, dynamic loading tests that create conditions for screw loosening are more desirable and can be more pertinent in identifying mechanical failure other than crack development. Four factors significantly influence fatigue failure in implant dentistry: the biomaterial, the geometry of the structure, the force magnitude and the number of cycles (Misch 1999a). Changes in the biomaterial or structural design of an implant or implant assembly can therefore be tested using the variables of load application and number of cycles.

Current International Organization for Standardization (ISO) guidelines for the fatigue testing of dental implants (ISO 14801) suggest that testing is carried out for the worst-case situation within the recommended use. The specimen has to be either rigidly mounted or within an embedding material with a modulus of elasticity higher than 3 GPa and at a 30° inclination. The fixture should be clamped at a distance 3 mm apical to the nominal bone level with loads applied through a hemispherical loading member not exceeding 15 Hz. A load-cycle diagram needs to be generated that shows a lower limit at which at least three specimens survive and none fail in the specified number of cycles (2×10^6 for tests conducted at ≤ 2 Hz, or 5×10^6 at < 2 and > 15 Hz). The standards suggest that an appropriate starting load is 80% of the load to failure in a static test performed using the same test geometry, and that at least four load conditions are used. Although these requirements, together with an assurance of good manufacturing practice, may satisfy standards and regulatory organisations, the conditions for an in-depth analysis of the mechanical behaviour of dental implant assemblies from a material testing perspective may differ.

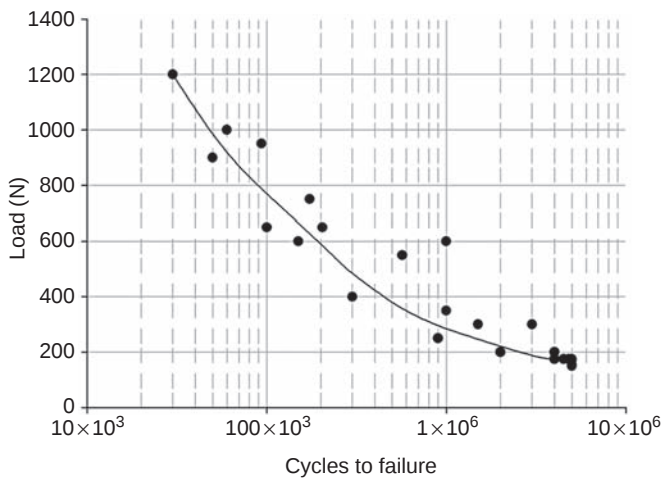
To establish the fatigue characteristics of an implant assembly it is essential to identify the load amplitude, spectrum, cycles and geometry, and the method of mounting of the fixture component of the assembly. These conditions can be inextricably related and test conditions need to be established appreciating the inter-relationship of the individual factors.

Load amplitude

Most test conditions are based on the application of a constant uni-directional dynamic load, commonly sinusoidal, between a nominal peak value and within 5% of this value. Uni-directional loads do not, however, simulate the clinical setting where a more complicated pattern of randomly varying stress amplitudes and frequencies exists. Rotational models (Basten *et al.* 1996) can be used to try to refine the test conditions although it would be desirable to have testing machines capable of alternating rotating and

bending forces to allow approximation of 180° force-field vectors. However, accurate data relating to the force vectors in the mouth are still lacking (Lang *et al.* 1999). Although uni-directional loads may be limiting, this approach can allow for the establishment of tests where the loading conditions can be set to a closer tolerance. Implant assemblies under dynamic testing can show a degree of 'spring-back' which can lead to practical problems of friction and machine shut down if the trip tolerances are low, especially when more sophisticated mounting apparatus and test conditions are used. A constant-load method also allows determination of the average life and average strength. Conventionally, a number of assemblies are tested at various stress levels until failure. The results from the cyclic loading tests are then used to produce a load-cycle curve based on a plot referred to as an *S-N* diagram (stress-life) (Fig. 14.21). This plot is based on the fact that known inter-relationships indicate that heavy loading will cause failure after a few cycles, while the material might sustain up to 10^6 or an infinite number of cycles if the load is decreased.

Random-load experiments may be useful for dental implant assemblies. This method is based on applying loads whose amplitude and frequency vary randomly with time. Such tests are commonly used to predict the service life of automotive and aviation components. By definition, however, random implies unpredictable and the most appropriate way to treat the random-load spectrum is to express it in terms of its statistical properties. A more manageable method would be to use a block pattern. A pseudo random loading spectrum can be established using a series of load,

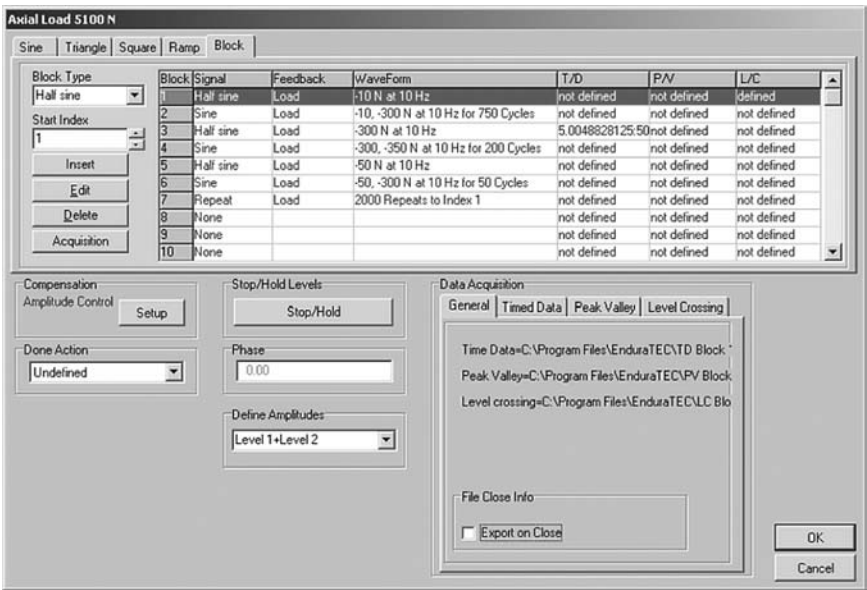


14.21 Example of *S-N* diagram generated for 3.3mm dental implant assemblies.

frequency and cycle combinations, and this block is repeated over a test period (Fig. 14.22). Recent developments in equipment and software technology have led to the development of chewing simulators for dental material testing. These have a bi-axial testing configuration where the masticatory cycle is characterised into: the preparatory phase during which the mandible is positioned, the crushing phase and the grinding phase. The ability for these phases to operate under different system control modes can allow for multi-axial control and synchronisation together with the ability of the apparatus to work in displacement and load control modes. The complex nature of loading and displacement can create operational problems and the frequency of testing may need to be limited to 2 Hz or less.

Load spectrum

The lack of consistent data on the forces generated in the various zones of the mouth can have a direct effect on any study that is aimed at investigating the ability of a biomaterial to withstand oral forces. One can therefore scientifically justify mechanical testing across a wide and excessive range of loading values in order to ensure that the potential loads experienced



14.22 Example of a block loading pattern. Cyclic testing machines can be programmed to deliver varying loads for pre-determined cycles on a repetitive basis to simulate the effect of parafunction or random loading.

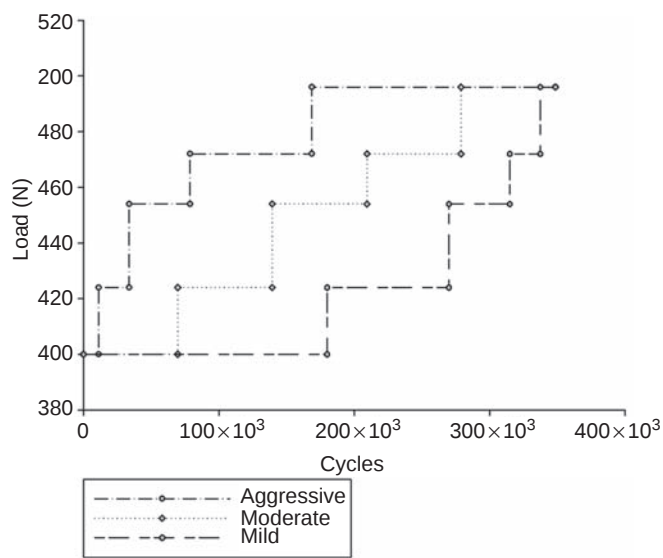
within the oral cavity sit within the spectrum used. Dental implant assemblies can show incredibly high levels of endurance at loads well within the yield strength of the assembly and it becomes important to base the load application to allow for a predicted event to occur within a realistic time frame, with the aim of making that event predictable.

The compressive bending test is commonly used in material tests, to determine an initial load within the proportional limit for cyclic loading. Dental implant assemblies can differ in this respect. As a static test, it predominantly tests the yield characteristics of the abutment screw. In an assembly with adequate torque application, the screw is protected from loads by the clamping force. Primarily, the application of load would lead to a decrease in the clamping force present in the mating components (Misch 1999a). Increases in the magnitude of load beyond the clamping force of the joint would primarily result in a small increase in screw tension within the elastic limit of the screw. Further increase of loading would result in a loss of preload followed by screw-joint failure. Aggressive loading conditions can be justified in any preliminary tests so that different modes of failure can be identified. This can allow for realistic further testing as well as acting as an initial reference point for any clinical complications subsequently encountered.

One of the problems in generating an $S-N$ data curve in high-cycle test conditions is that run-out tests can often occur with no failure experienced. Such data points are normally indicated on a plot with an arrow. A disadvantage of this method is that no information can ever be gained on whether these samples would have ever failed. An alternative test method, which results in a data point for each test, is the step-stress loading method (Nicholas 2002). This method offers great potential for improvements in reliability demonstration bench testing and can be an efficient tool to assess life distribution for highly reliable products. In contrast, life testing can be a lengthy procedure with results generally becoming available too late to be of much use. Step-stress testing can be achieved by testing an implant assembly at stress levels greater than operational levels in a stepwise fashion (Fig. 14.23) to reduce the time-to-failure (Lee and Lu 2006). For ferrous materials, however, it has been noted that materials can be made to withstand stresses higher than the conventional fatigue limit when they are exposed to periods of cycling in steps of increasing magnitude. This phenomenon is known as 'coaxing'. This effect has not been demonstrated in titanium alloys (Nicholas 2002).

Load cycles

Accurate data quantifying the number of chewing cycles of an average individual over a period of years would be useful to determine the number



14.23 Step-stress loading profile for accelerated testing.

of load cycles that should be applied to a dental structure during mechanical testing. Assumptions can be made that three periods of 15 minutes chewing per day at a chewing rate of 60 cycles per minute amounts to roughly 10^6 cycles per year (Wiskott *et al.* 1995). Not every chewing cycle is, however, active and if the number of cycles is decreased to more realistically represent approximately 10 minutes a day, then 10^6 cycles can be equivalent to 5 years' wear of the mouth (Murphy 1965). Parafunctional events such as bruxism can alter this. Although individual variation occurs, increase in tooth contact can be of the order of four times the norm with up to 40 minutes contact per day, usually within an 8-hour sleep period.

Determining the number of load cycles therefore becomes dependent on the load selected as well as the nature of the test to be run. Alternatives to catastrophic failure or sample run-out would be to use combinations of material tests based on subjecting the implant assembly to a cyclic load challenge and to evaluate the effect of such a challenge by other bench test means such as loosening torque. Such tests may be more suited to assessing screw-joint performance.

Accelerated test methods can also be applied to implant assemblies. This method is based on increasing the intensity of the load condition to reduce the testing time. Accelerated methods can be used to meet the test objectives within a shorter period of time or if there are a limited number of samples to be tested. An important caveat is that the mode of failure under

accelerated conditions should be the same as under anticipated normal operating conditions. Analysis of the data from small-sample accelerated tests can be achieved by applying the principles of Weibull distribution both for failure forecasting and failure analysis (Abernethy 2005). Accelerated testing can therefore offer an alternative to the staircase method of testing. The latter relies on an estimation of fatigue strength for a desired life and the first test run determines whether the load for subsequent tests is increased or decreased. The staircase method does, however, require a large sample size (>20).

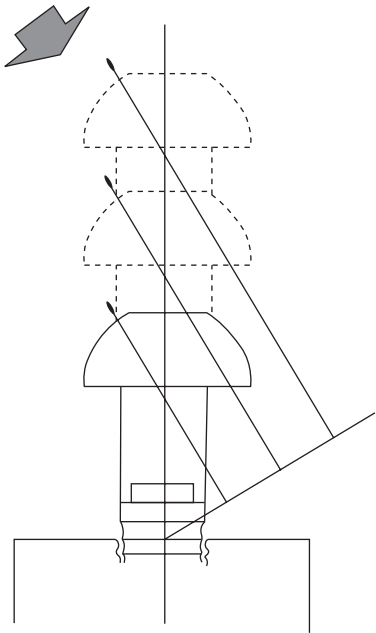
Load geometry

The direction and distance of loading in relation to the implant assembly can have a bearing on the results obtained from cyclic and other forms of bench testing. Varying the angle of load application will vary the relative vector components of axial, transverse and bending force. Clinically, most critical types of load involve some element of a bending moment and therefore test conditions should attempt to recreate such loads either by sufficiently off-setting a vertical load (Binon 1996a) or by introducing angulation into the test conditions (Boggan *et al.* 1999). The bending moment experienced by an implant structure is dependent on the physical relationship of the magnitude of force applied and the length of the lever arm, which can be dependent on the direction and distance of the force above the fulcrum. Although an abutment height of 8mm has been universally accepted for material testing (Balfour and O'Brien 1995; Binon 1996a; Boggan *et al.* 1999), within the clinical setting, it is possible to be confronted with clinical situations where, due to marginal bone loss, the proposed level of the head of the fixture may give rise to restoration lengths in excess of 8mm. In such situations, the whole implant pillar would be subjected to bending moments relative to restoration height. The variance in restorative height can therefore have a significant effect on the performance of an implant assembly. An increased restoration height creates a greater challenge on the clamping force of the joint and the preload within the abutment screw. Using test assemblies of varying heights (Fig. 14.24) can facilitate the analysis of the effect of increasing the lever arm on the implant components (Fig. 14.25).

Load geometry can also be affected by the level at which a fixture is mounted within an assembly. The ISO guidelines are aimed at replicating the worst-case scenario with performance based on aggressive bone loss of 3mm apical to the manufacturer's nominal level. Within a clinical setting, the majority of dental implants are unlikely to show that degree of bone loss. In view of this, it can be considered reasonable for fixtures to be mounted at a level best suited to the investigation proposed. A greater exposure of the fixture above norm would subject areas of the fixture to



14.24 Test assemblies at varying restorative heights.



14.25 Lever arm at varying restorative heights.

loading, possibly provoking implant fractures (L. Jorneus, personal communication, 1999). Totally embedding the fixture into the mounting medium would place greater emphasis on the performance of the abutment–implant junction.

14.7.7 Loosening torque tests

Loosening torque tests can be carried out where the torque required to loosen a screw is measured. They have been shown to reflect the loss of abutment screw preload following function and can be used to quantify the effect of loading an abutment–implant complex. The removal torque of a screw is usually lower than the tightening torque and can depend on the material used. Gold alloy abutment screws would appear to require approximately 75–80% of placement torque to remove them (Haack *et al.* 1995). Implant systems based on a cone-screw abutment connection have shown the loosening torque to be 80–85% of clinically relevant levels of tightening torque. The presence of a cone within such connections does seem to affect the loosening torque value (LTV). In some cases, the LTV can be 104–124% of the tightening torque (Sutter *et al.* 1993; Suleiman 2006). In situations where the implant assembly has been subjected to forces, removal torque tests can be used to evaluate the loss of preload based on the above premise (Dixon *et al.* 1995). The reduction of torque noted on loosening is unlikely to be deleterious if it is not progressive, as long as the remaining clamping action is sufficient to prevent slippage within the joint (Breeding *et al.* 1993). An unknown factor is the degree of preload or residual torque required in a screw joint to resist loosening, particularly in relation to masticatory forces and adverse bending moments.

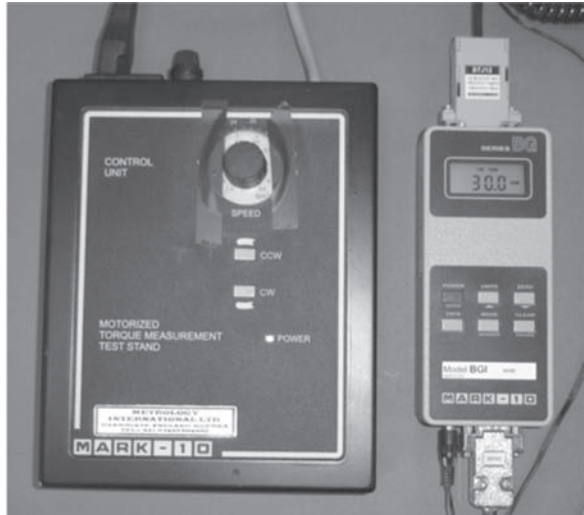
Various types of hand-held torque gauges exist both analogue and digital. Analogue models such as the Tohnichi torque gauge (Model Number BTG36CN-S, Tohnichi NV, Ota-Ku, Japan) can verify the absolute torque applied or loosened but are limited in other forms of data collection. Digital torque gauges, examples of which are the Mark-10 torque gauges (Model BG1, Mark-10 Co., Hicksville, New York), can capture the peak torque in both directions and have selectable units of measurement. By using a data acquisition and device control interface software package (WinWedge 32 Pro, TALtech Inc., Philadelphia, Pennsylvania) real-time data can be captured allowing a more extensive analysis of the developing clamping force. For accurate measurement, it is important that the test assembly is centred within the gauge and that the device is held in an upright fashion (Fig. 14.26).

Torque test stands (Model ESM, Mark-10 Co) can be of benefit in ensuring that the sample is correctly positioned for the torque test. The motorised capability allows for the test to be operated at variable rotation speeds of

(a)



(b)



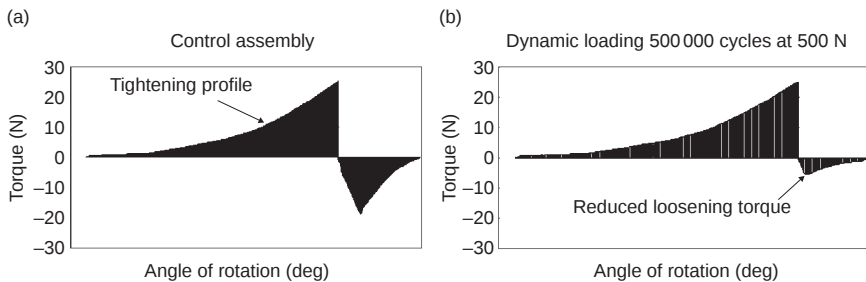
14.26 Torque tests with a digital gauge and motorised drive. *a* The test assembly should be mounted in the true vertical when applying torque. *b* The use of a motorised apparatus standardises the rate of torque application.

13–330 mm/min allowing for a standardised technique to be used from one test assembly to another. Another feature of the motorised stand of importance is the ability to measure the number of rotational degrees a screw travels through in the process of tightening to the recommended torque level.

14.7.8 Torque–angle signature analysis

By standardising the application of torque to an assembly and by collecting the data mentioned above it becomes possible to verify the tightness of a screw using torque–angle signature analysis (TSA). In addition, the characteristic of a screw can be determined and comparison of its performance against other screws of differing materials or design can be made. Traditionally, torque measurement has been used to determine the optimal assembly of a bolted joint. It is a practical and relatively easy measurement method either dynamically during the tightening process or in a post-assembly audit. In critical joints, however, it may not be sufficient to measure solely the torque applied. The process of tightening a screw can be defined in various stages. Primarily, there is an aligning

period during which the screw aligns the parts and draws them together. An elastic clamping stage during which the joint has been stabilised and the screw is ‘snugging-up’ the joint follows this. Torque application is usually at a level of 75–80% of yield strength of a screw and hence this point should lie within the elastic clamping zone. If torque application is viewed as a process of energy transfer then in the above sequence not all the energy applied gets transferred into preload. A variable amount of energy is used in overcoming the friction of the two parts when tightening the screw and, hence, the clamping or preload established may not be representative of the torque applied. It has been stated that the majority of the energy applied goes into overcoming the friction that exists under the screw head (50%) and within the threads (40%), potentially leaving a residual of 10% of the energy to be transferred into clamping force (Source: RS Technologies Ltd website). What would appear to be a more accurate measure of the clamping force would be to measure the angle of rotation of the screw, as this measurement is more directly proportional to the clamp load than the measurement of torque. The significance of the method lies in defining the relationship of the screw rotation to clamp load. The angle of rotation can then be used to predict the amount of clamp load with the intention that the screw can be tightened to a preliminary torque, allowing all the components to be aligned, and the screw can then be rotated a specific angle to produce the correct clamp load (Miller 2007). TSA also has diagnostic value as it allows the characteristic of an assembly to be evaluated to determine if underlying problems exist within an assembly, its embedment features and screw features. This method is a relatively new development within the engineering world and has only recently been introduced into testing dental implant assemblies (Fig. 14.27).



14.27 Torque signature analysis plots. Torque applications under control conditions create a tightening profile and loosening torque value of approximately 75–80% (a). Following a strength challenge the loosening torque value is diminished and can be characterised (b).

14.7.9 Combining mechanical test methods

Existing single mechanical test methods have shown that results can be obtained on the strength of an implant–abutment connection and insight can be gained into strength characteristics. However, many of the conventional tests can lack the sensitivity required to detect joint deterioration under test conditions. As most dental assemblies are based on the mechanical principles of a threaded bolt, combination test methods can give greater insight into screw-joint performance. Assessing preload before and after a test involving strength challenge can help to quantify loss of preload and the effect this may have on future screw loosening. Although preload may not be directly measured, it is accepted that LTV and torque audit analysis can be representative of the loss of preload.

14.8 Stress analysis of the bone–implant interface

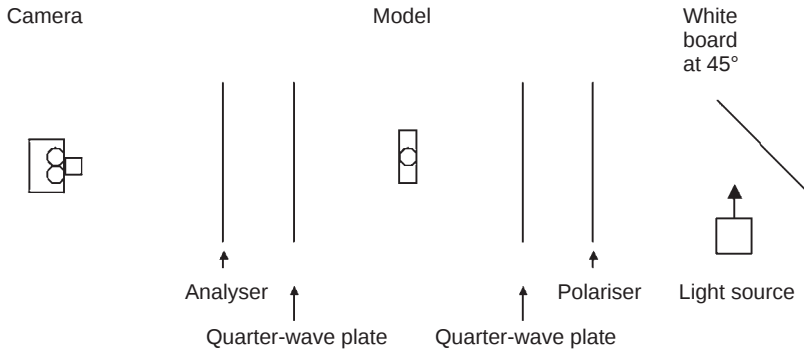
The role of the dental implant is to transfer the mechanical forces created during chewing to the supporting osseous tissues within the mandible and maxilla (Inan and Kesim 1999). It is of benefit to evaluate the effects of stresses exerted on the supporting bone as a result of the stress and strain fields around a fixture (Rieger *et al.* 1990a). At present, there are no *in vivo* techniques that allow for an accurate realisation of stress, although numerous physical and theoretical methods are available to analyse stress distribution for complex structures *in vitro*. The aim of *in vitro* testing should be to replicate wherever possible the conditions relating to mechanical and biological failure using models representing the clinical situation. The problem that exists is whether or not the *in vitro* models can relate accurately to the *in vivo* condition. Stress analyses tests are used commonly to evaluate the load transmission from an implant to the surrounding tissues in an effort to understand biological failure, and various models exist using techniques such as finite element stress analysis and photoelasticity. Historically, stress analysis methods have included strain lacquers and elapsed-time holographic interferometry although their use can be considered dated and there has been no validation of this method for analysis of dental components.

There are an increasing number of studies targeting the causes of failure in clinical practice using various stress analysis methods. The major expectation from these studies is to extrapolate findings relevant to the risk factors instead of discovering these factors by clinical experience. Biomechanical principles and their application to dental implant structures, therefore, have to be the focus of stress studies (Akca and Iplikcioglu 2001).

14.8.1 Photoelastic stress analysis

Photoelasticity is a technique used in stress analysis testing based on the ability of a transparent non-crystalline material that is isotropic when free of stress to become optically anisotropic displaying stress characteristics when stressed. These characteristics persist while loads are maintained but disappear when the loads are removed. When a photoelastic material is subjected to load and viewed with polarised light, colourful patterns are seen which are directly proportional to the stresses and strains in the material. The method was developed at the turn of the twentieth century and found widespread use in many industrial applications as it exceeded all other techniques in reliability, scope and practicability. The process consists of embedding a dental implant within a coating material manufactured with a controlled formulation of resins blended to provide known and repeatable properties. As the photoelastic coating is intimately and uniformly bonded to the surface of the implant, on load application the strains are faithfully transmitted to the coating. The method has the ability to demonstrate the quality, quantity and distribution of force around an object by means of fringes that appear as a series of successive and contiguous bands. Interpretation is based on the principles that the larger the number of fringes, the higher the stress magnitude and the closer the fringes are to each other, the higher the stress concentration. The nature of the fringes is both isochromatic and isoclinic. Various models can be used to study fringe patterns. Two-dimensional techniques rely on models created from sections of a structure under test. Fringe patterns are based on planar stress distribution. Three-dimensional analysis requires sectioning the model after each load sequence. Sequential loading tests require the production of multiple models making comparable analyses difficult, as different inherent stress patterns would exist in each model produced. The load transfer characteristic of implants can be studied using the quasi-three-dimensional model. This allows for the model to be constructed maintaining the structural integrity of a fixture and for the model to remain intact after each loading sequence. The quasi-three-dimensional model can be relevant to single- or multiple-implant test models.

Photoelastic models have to be viewed through polarised light. This can be achieved by using either a plane or circular polariscope. The preferred method is based on the circular polariscope, which introduces further polarising filters known as ‘quarter-wave plates’ thereby restricting the display to isochromatic fringes. A schematic of the polarising set-up is shown in Fig. 14.28. Fringe generation occurs when an unloaded model is incrementally loaded. Fringes first appear at the most highly stressed points and as the load is increased new fringes appear, pushing the earlier fringes towards areas of lower stress. This process continues until the maximum



14.28 Photoelastic lighting arrangement.

load detectable by the photoelastic material is reached. Each fringe can be assigned an ordinal number and they retain their individual identity ('orders') throughout the loading sequence. The benefit of the analysis is that each fringe is not only ordered, and always maintains its respective position in the ordered sequence, but is also orderly in that each is a continuous contour highlighting the same principal stress magnitude. The different fringes never cross or merge.

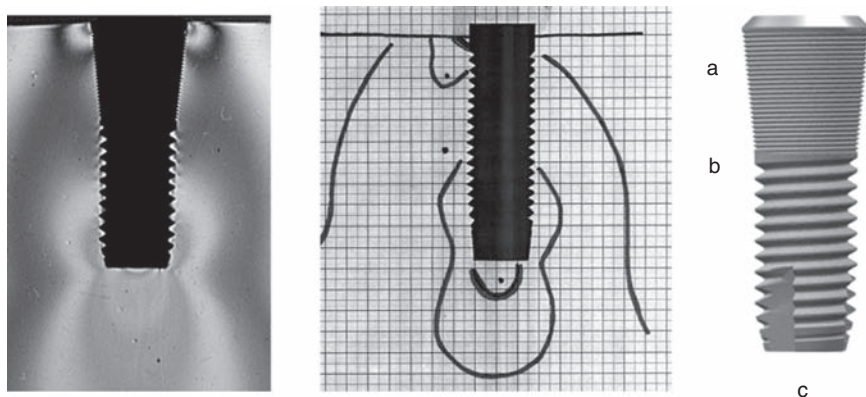
The photoelastic technique is not without its limitations. Bone consists of an outer cortical plate and an inner cancellous section. The material properties and characteristics are known to be different. Although the modulus of elasticity of photoelastic resin is similar to that of cancellous bone, the resin is a homogeneous substance and hence the stress patterns around an implant in this medium are likely to be more consistently distributed than in bone, allowing for controlled comparisons in different loading conditions. The homogeneity of the resin may mean that the magnitude and pattern of stress may be different from that of real bone. Using plastics of different modulus to simulate cortical and trabecular bone can create composite photoelastic models. Analysis of these models can show a different distribution of fringe patterns that is possibly more realistic to the clinical condition (Jeong *et al.* 2003). An implant, particularly in the partially dentate patient, is placed within the boundaries of other teeth and surrounded by varying amounts of buccal, lingual and marginal cortical bone that can influence stress distribution. Differences in fringe pattern generation can be highlighted by comparing photoelastic models of a single implant and that of an implant interposed between two teeth. The production of photoelastic models is also a very technique-sensitive procedure. The polymerisation process can lead to the introduction of internal stresses that may not be entirely eliminated. These stresses can make accurate quantitative analysis difficult.

The extent to which the photoelastic method can be of benefit in stress analysis around a single implant remains debatable. Multiple-implant models can be generated in photoelastic resin in order to gain an insight into the implications of framework fit on stresses induced around implants. Distortions around cast, implant-borne superstructures can have an effect on stress distribution within the screws retaining the framework. In addition, when such a framework is torqued into position, undesired forces and moments can be applied to the implants resulting in undue stresses within the bone. Fringe pattern analysis in this type of model can give an insight into the distribution and magnitude of adverse stresses. Stressed photoelastic models can show adequate recovery if the load is removed and the model allowed to rest. This feature can help in repeated use of the same model under different test conditions enabling comparative analysis studies. Analysis needs to be based on evaluating the fringe patterns at designated points around a fixture (Fig. 14.29).

The photoelastic method has also been useful in situations where mathematical methods can become cumbersome, although the advent of superior computer processing power has meant that the finite element method has become the dominant stress analysis technique. Nonetheless, photoelasticity can still offer accurate rendition of critical stress points around materials of irregular geometry.

14.8.2 Finite element stress analysis

In recent years, the finite element method has been used to investigate stress analyses within implant dentistry. The National Agency for Finite

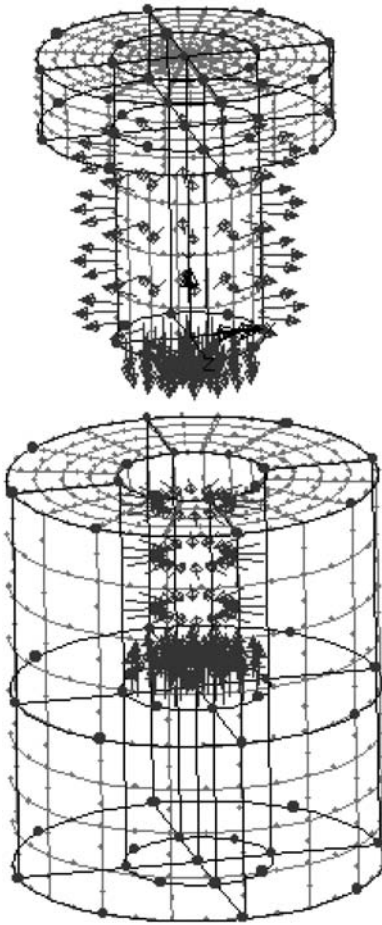


14.29 Method for photoelastic fringe analysis. Fringe orders can be recorded at pre-determined points (a, b, c) within the bone simulant to quantify implant loading.

Element Methods has defined finite element stress analysis as ‘a theoretical method that can be used for calculating the behaviour of a real structure by performing algebraic solutions of a set of equations describing an idealised model structure with a finite number of variables.’

Finite element analysis can provide a non-destructive system for quantifying stresses generated at the various interfaces of similar or dissimilar materials. The method is capable of simulating complex geometric shapes, material properties and various boundary conditions, which can be difficult to replicate in laboratory or clinical experiments (Huang *et al.* 2002). As a result, it can be seen as an ideal tool to investigate the functional responses of dental implants in different conditions. It allows the investigation of the relative merits of different parameters, shapes or designs as well as offering insight into the internal state of stress in components or materials within the implant or at the implant–bone interface. The mathematical relations for finite element analysis are based on standard matrix structural analysis methods where matrix operations are used to formulate the problems and solutions (Ural 1973). The development of computers has allowed the method to be developed further and with increasing computational power, more complex structures can not only be modelled in two and three dimensions but can also be analysed in increasingly shorter times.

The finite element method also allows for the study of the internal state of stress of components (Meijer *et al.* 1993) as well as the stress patterns in two or more dissimilar materials adjacent to each other without affecting their independent behaviour. This method is therefore ideally suitable for the biomechanical analysis of orthopaedic, cardiovascular and dental structures (Tuncelli *et al.* 1997). The method relies upon two concepts. Primarily, the structure under investigation needs to be divided (hypothetically) into a collection of much smaller and simpler domains known as finite elements. These should be small enough to allow approximation of the shape of the displacement or stress field, leaving only the magnitude to be determined (Geng *et al.* 2001). Secondly, the individual finite elements need to be connected together at nodal points such that the points can then be subjected to certain loading conditions resulting in the behaviour of the model being similar to that of the structure it represents (Tuncelli *et al.* 1997). The process of dividing the structure of interest into nodes and elements to create a mesh is referred to as discretisation and computationally a system of simultaneous equations is generated to relate all the forces and displacements at the nodes. The problem is therefore transformed into one of matrix algebra, the solution of which describes the displacements, strains and stresses within a structure (Holmes *et al.* 1997). Both two- and three-dimensional models, together with axisymmetric techniques, can be used although the three-dimensional model can offer a more precise prediction of stress distribution (Fig. 14.30). In particular, due to the non-destructive nature of



14.30 Three-dimensional modelling of an implant component.

the analysis, finite element analysis has become an increasingly useful tool for the prediction of effects of stress on a dental implant and its surrounding bone (Geng *et al.* 2001). The method has been used to evaluate the effect of various parameters including implant geometry, prosthesis design and load conditions on stress and strain distribution in the peri-implant region (O'Mahony *et al.* 2001).

Early efforts in the finite element method were method-oriented and not problem-oriented, with solutions generated without carefully formulating the problem. Progress towards closer and more precise definitions of the problems requiring solution by finite element analysis has meant that although many analyses have not led to solutions for realistic problems,

they have served to guide experimental biomechanical research in areas of material testing and functional force evaluation. In these fields, utilising a problem-oriented approach, the finite element method can play a significant role with models that do not need to be complicated in construction (Huiskes and Chao 1983). Creating a model for analysis by the finite element method primarily requires the structure to be divided into finite elements and then idealised into some form of a mesh. This process relies on approximation and the consequences of these approximations have to be understood in order to minimise their effects within the solutions reached.

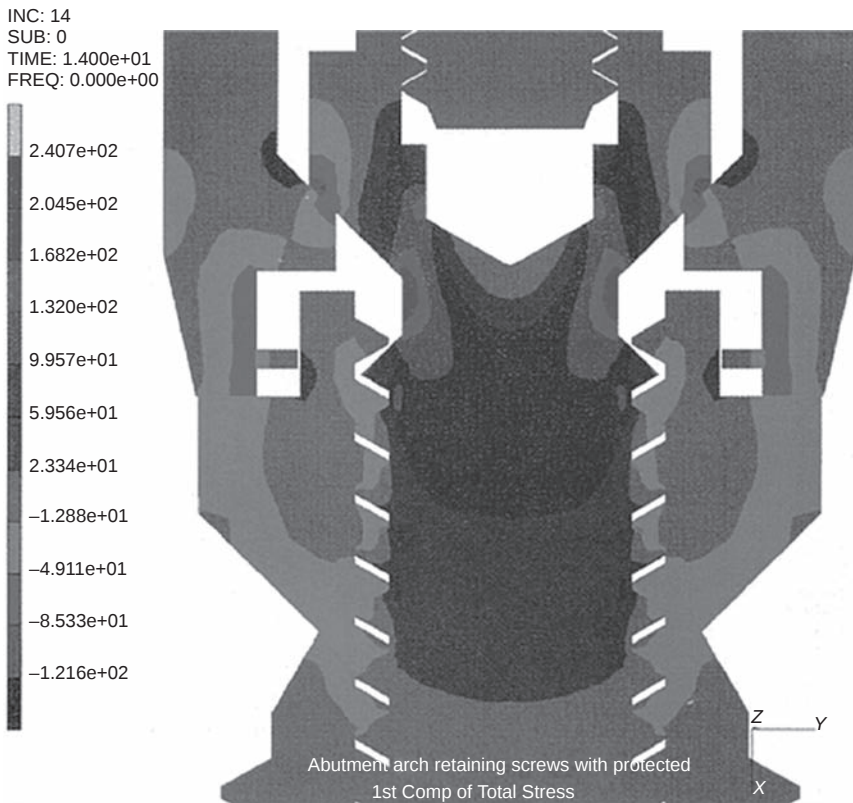
However, problems do exist with experimental analysis of any nature. The limitations of finite element analysis mean that the analyses have to be based on certain assumptions and approximations to enable the modelling and solving process to be carried out. The validity is therefore dependent on the nature of the assumptions and it becomes important to evaluate the modelling method and the sequence of analysis to evaluate the results that can be obtained. The principal difficulty in simulating the mechanical behaviour of dental implants in finite element studies lies in the modelling process. Knowledge of the biological geometry and material properties of human bone tissue and its response to applied mechanical force is not comprehensive (Geng *et al.* 2001). There appears to be a considerable difference in the understanding of the physico-chemical nature of the bone–implant interface (Huja *et al.* 1998; Van Oosterwyck *et al.* 1998; Chen *et al.* 1999). The masticatory forces that are generated are typically three-dimensional with components directed along one or more of the clinical co-ordinate axes. *In vivo* they are cyclic and dynamic and these features need to be modelled so that the load cases applied can represent the direction, magnitude and nature of loading likely to affect implant stability. In finite element models, conditions need to be attributed to the bone–implant interface. As the exact mechanical properties of the interface have not been clearly defined, various assumptions have to be made and varying results can be gained. The interface between the implant and bone is generally modelled in one of two ways. It can be considered as a free contact or a fixed bond. Relative displacement with no resistance to tensile force can be allowed within a free contact and many smooth, machined implant surfaces have been modelled using this assumption (Akca *et al.* 2003). On the other hand, a fixed bond can be modelled with an infinite strength in tension and shear to simulate ideal osseointegration (Rieger *et al.* 1990a; Stegaroiu *et al.* 1998). This can be represented in a finite element model by a higher friction of coefficient acting at this interface (Vaillancourt *et al.* 1996). A fixed bond can also prevent any relative motion between bone and implant under loading (Meijer *et al.* 1996). Bone bonded modelling can also be used to represent implants with bioactive coatings and roughened implants created by grit blasting or acid etching (Rieger *et al.* 1989; Hansson 1999). The results

generated by finite element analysis can vary depending on the nature of the interface modelled. It can be possible to demonstrate a two- to five-fold increase in the values of maximum compressive stress adjacent to an unbonded implant when compared with a fully bonded implant (Siegele and Soltesz 1989). In general, it is important to define the contact between bone and implant with non-penetration constraints keeping both aspects deformable (Van Oosterwyck *et al.* 1998). Although the pure sliding contact and the bone bonded models can be separately described, it may be possible that these interfaces occur simultaneously in different regions of the interface in the clinical situation (Buchler *et al.* 2003). Modelling the implant can be aided by product descriptions that state accurately the specification of the components. Certain modifications, however, are commonly carried out in studies to simplify the calculation process. As most implant fixtures are manufactured with continuous screw thread designs, modelling thread characteristics can be an important factor. The assumptions assigned to the interface condition can be of importance. With some interface conditions the presence of threads can have little effect on the overall stress and strains, and modelling can be simplified to purely cylindrical reconstruction (Clelland *et al.* 1993). To replicate the potential clinical condition, it can make sense to model threads that engage bone and hence have a role in resisting displacement (O'Mahony *et al.* 2000). Continuous screw threads can be difficult to reproduce and they can be commonly remodelled as concentric circles in fixtures and other components (Kunavisarut *et al.* 2002) for computational analyses, with the assumption that the stresses are not significantly affected by this design (Rieger *et al.* 1990b). However, it can be viewed that stress distribution in threaded connections is important, as are specific thread details. Thread form, pitch, number of starts and nominal diameters can alter the stiffness of the threaded connection and affect the possibility of screw loosening or fatigue failure (Johnson 2002). Differences in modelling implant shapes can also affect results based on interface conditions.

While the focus of analysis is on the stress distribution within bone, the design of the implant–abutment interface can be simplified to a rigid fixation with the abutment modelled as an extension of the implant (Clelland *et al.* 1991; Canay *et al.* 1996; Sertgoz 1997; O'Mahony *et al.* 2000). It is also possible to have abutment components separately modelled with a rigid connection (Holmes *et al.* 1997). Both types of modelling are likely to have little significance when models are axially loaded and the analysis restricted to that of stress distribution within the bone. In analyses where the model is subjected to non-axial loads, the effect of a rigid continuation of the implant into the abutment has the benefit of allowing cantilever-type loads to be applied. However, it is known that stresses can exist within the implant–abutment connection and hence in most cases it would be

important to observe the effect the loading has on the implant–abutment junction. In the absence of an accurate design of the implant–abutment junction, these stresses would only be able to reflect the geometry of the model and not be representative of the true connection. Without accurate and representative geometry for this complex, it becomes difficult to analyse the area for any internal stresses and the resultant effects of masticatory loading.

Problems can exist in modelling the implant–abutment junction. The geometry of such a junction is quite complex with many areas of dead space, screw threads and internal faceting. Nonetheless, finite element analysis can be considered a valid scientific approach to determine the effect of varying certain features of an implant–abutment connection to try to establish the parameters that may be relevant to joint strength, and to assist in the production of a more optimal design (Fig. 14.31). Boundary conditions need to be established in any finite element analysis. Analysis of stresses or strains



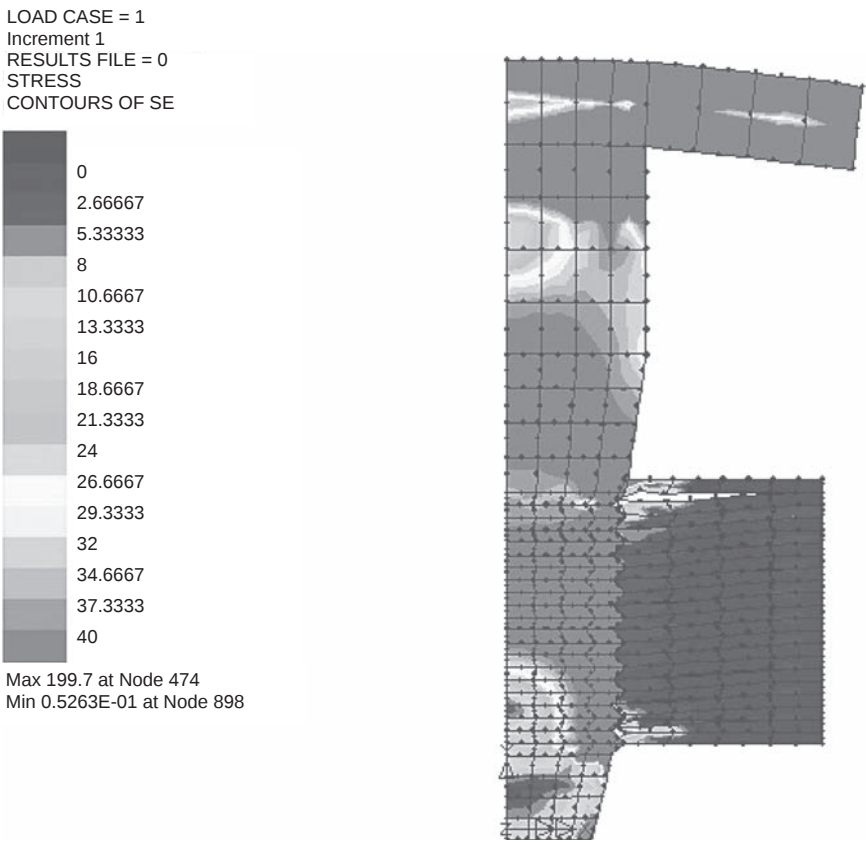
14.31 Axial stresses within the implant–abutment complex (reprinted from Sakaguchi and Borgersen 1995 with permission).

in any structure requires that the laws of equilibrium, motion and strain compatibility be followed. The boundary of the model has to be attributed conditions that support either a complete model or a section of the structure under analysis. This may involve restraining any displacement as would be expected in the real-life situation. Without restraint, the computational analysis would carry on infinitely and not converge to a solution. The finite element method can accommodate large varieties of loading conditions and the direction of loading can also be varied. In many circumstances, particularly in linearly elastic materials, the effect of any force can be simply computed if the effect of the unit force is known. In effect, this means that unit-static loads (1 N) can be applied (Stegaroiu *et al.* 1998). This is based on the direct proportionality between loads and stresses if the theory of elasticity is applied, provided that the deformations and displacements are not so large that the geometry of the structure is changed (Hansson 1999). Forces applied to models can be idealised as normal point loading. This can lead to a concentration of stresses under the applied load and results in this region need to be ignored as they occur due to the mathematical idealisation of the model. In reality, masticatory forces are actually spread over a region as opposed to occurring at one point (Lewinstein *et al.* 1995). It is also possible to model axial loads with loads applied at an oblique direction of 30° (Papavisiliou *et al.* 2005) or in a horizontal direction (Abu-Hammad *et al.* 2000). Off-axial loading can also be simulated by applying a load and a bending moment directly to an abutment crown at designated distances lateral to the long axis (O'Mahony *et al.* 2000). Simplified simulation can also be carried out by analysing the vertical and horizontal components separately (Abu-Hammad *et al.* 2000).

Mechanical testing of dental implants can be limited by the fact that commonly only one specific test can be carried out on the experimental set-up at a given time, and also by the inability to re-use components that have been through test procedures. In addition, the design, prototype and re-design test cycle can be time-consuming and costly. In contrast, the finite element method is capable of being applied to many different forms of analysis based on the material, the desired investigation and the nature of the test. The nature of modelling can allow analysis in numerous directions. With axial loading, analysis of the bucco-lingual section can be made and assumed to be equivalent in all radial directions. With oblique loading, more information can be gained by analysing in both bucco-lingual and mesio-distal directions (Lin *et al.* 2000). The numerical values gained are mathematical calculations without variance and hence statistical analysis is not required (Akca and Iplikcioglu 2002). The stress distribution pattern of choice is usually the von Mises stress value as it best represents the bi-axial stress state that is commonly modelled. It is calculated from the six stress components normally present

in three-dimensional stress analysis of homogeneous structures (van Zyl *et al.* 1995).

The von Mises yield criterion is based on an internal energy concept. Failure occurs when the von Mises stress value exceeds the material yield strength of the implant material. The material therefore no longer behaves elastically and deforms permanently (Lewinstein *et al.* 1995). The criterion may also be used to predict which component is most likely to fail (Murphy *et al.* 1995; Kunavisarut *et al.* 2002). In effect, von Mises stress values define the beginning of deformation for ductile materials such as metallic implants. This analysis can be important in interpreting the stresses that occur within the implant material and components (Fig. 14.32). Finite element analysis can, however, give the impression of extreme accuracy because of the math-



14.32 Von Mises stress values for off-axis loading. Two-dimensional static model depicting von Mises stress values resulting from application of load and bending moments lateral to the long axis (adapted from Murphy *et al.* 1995).

ematical calculations that can be presented in a study. However, care must be taken in evaluating the absolute values generated in a calculation, as the stress values that actually cause biological changes such as resorption and remodelling in bone are not known. In addition, the values of stress provided by analysis, in view of the inherent limitations, are not necessarily identical to actual ones.

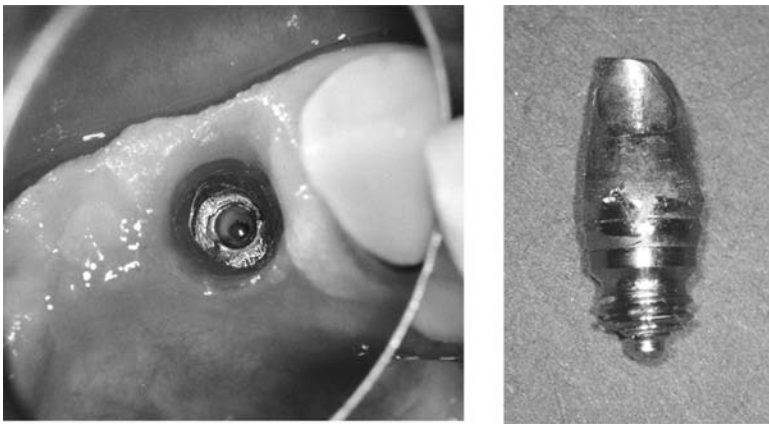
In summary, it would appear that the limitations related to the geometry of bone and implant structures in finite element modelling can affect the validity of results obtained, as they cannot be supported by experimental approaches (Pietrabissa *et al.* 2000). Results can also be affected by the assumptions that need to be built into the analysis, particularly the properties of bone, making either averaging or evaluation of worst-case scenarios necessary (Kim *et al.* 1999). This means that although finite element results can have limited quantitative significance, qualitative conclusions can be considered valid results of an analysis. It can be said that the true value of finite element analysis in testing dental implant assemblies can only be appreciated when the tool is used with bench test methods. While mechanical testing can determine if and when an assembly will break, the finite element method can provide an insight into the inherent mechanics of a given technical system by depicting the internal stress of a situation and by exhibiting the location of any weaknesses (Merz *et al.* 2000).

14.9 Summary

Under ideal clinical conditions, dental implants can survive for considerable periods with good bone maintenance, stable soft tissue and component integrity (Fig. 14.33). With product and design developments, technical complications associated with components, such as screw loosening, can be infrequent. All components, however, can be susceptible to fracture with devastating consequences for the patient. Studies have shown that implant fracture rates of 0.4% can exist at five years (Fig. 14.34) increasing to 1.8% at 10 years (Pjetursson *et al.* 2004). Within the implant stack, the mean incidence of fracture for the abutment screw has been reported as 2% with gold retaining screws showing an incidence of 4% (Goodacre *et al.* 2003). In view of the potential for complications, the *in vitro* testing of dental implant assemblies can be justified, particularly if the laboratory tests can offer a predictive value relating to clinical complications (Wiskott *et al.* 2007). The benefit of laboratory testing lies in the ability for individual aspects of an assembly to be tested and analysed without the confounding variables of the biomechanical properties of bone, the effect of the oral environment and characteristics of loading that exist within the patient population. The nature of laboratory tests that should be carried remains under discussion with proponents for simple testing methods or



14.33 Single-tooth implant restoration.



14.34 Implant fracture after six years' clinical service.

the use of techniques that can replicate certain aspects of human function. Load application in fatigue testing is one such example. Many current tests are carried out using unilateral loading conditions. Studies have also adopted methods that aim to duplicate the multi-vectorial force pattern of the mouth by configuring test assemblies as rotating cantilever beams (Wiskott *et al.* 2007).

Under ideal circumstances, the results obtained through laboratory testing should assist manufacturers and clinicians alike in making long-term decisions based offering a system design and treatment modality that can ensure that patients receive implant treatments that can stand the test of time.

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Superplastic forming of dental and maxillofacial prostheses

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15.1 Introduction

There is a continuous demand for dental and maxillofacial prostheses resulting from both disease and trauma. Specifically, the main causes of skull defects requiring implants are reported to be severe intracranial traumata, tumours, cerebral infarcts and osteomyelitis (Wehmoller *et al.*, 2004). Cancerous tumours often account for the necessary removal of significant amounts of hard and soft tissues in order to prevent the disease from spreading and surgery is a major treatment option. In such cases, significant reconstruction may be required to allow the person to return to as near normal living conditions as possible. Such reconstruction can often involve the use of biomaterials that ideally would integrate with the tissues and perform in a manner that would illicit an appropriate host response. Ideally, the appropriate response would be site specific.

The biomaterials that have been used for such reconstructions are many and include materials from the major classes – namely metals, polymers and ceramics, and various composites of these. The properties of such materials vary considerably and some are more ideal than others for specific implant types. For example, the ideal properties of a biomaterial for craniotomies have been reported to be inert or biocompatible, non-thermal conducting, radio-transparent, non-magnetic, light-weight, with appropriate physical and mechanical properties, and economically viable (Wehmoller *et al.*, 2004). In this situation, however, it is still the case that metallic alloys, and particularly titanium alloys are widely used, in both the commercially pure and the Ti–6Al–4V alloy forms, for this and several other maxillofacial hard-tissue reconstructions including malar augmentation and orbital floor reconstructions.

It has already been explained that the range of metallic alloys used for surgical applications includes commercially pure titanium and the

Ti-6Al-4V alloy. Titanium alloys have some of the best biocompatible properties of all metallic alloys and, for this reason, many dental and medical implants and devices are manufactured from these grades. Other properties that make these alloys good for surgical use are the relative transparency on plain x-rays, which leads to minimal artefacts on computed tomography (CT) and magnetic resonance imaging (MRI). As a result, titanium is a good material for implantation and radiographic follow-up. Moreover, among the biocompatible metals, titanium has the lowest Young's modulus ($115\,000\text{ MN m}^{-2}$). Thus titanium is a very favourable material for the reconstruction of hard tissues. Furthermore, the yield stress of titanium varies between 200 and 890 MN m^{-2} and the tensile strength between 290 and 930 MN m^{-2} , depending on the grade of the titanium (Pattijn *et al.*, 2002). The lower strengths are found for the commercially pure grades 1–4 while grade 5 (Ti-6Al-4V) exhibits the higher strengths.

When manufacturing with these grades of titanium alloy, the purer grades (CP grades) would be expected to show elongations of up to 50% over a 50 mm length. However, interstitial impurities have a strong influence on tensile properties; for example, 0.15 wt% nitrogen can reduce the elongation to 30% (Boyer, 1993c). Usually, the expectation would be that the alloy grades would show reduced ductilities compared with the CP grades, and at room temperature Ti-6Al-4V alloy typically exhibits 10–14% tensile elongation, in keeping with expectations (Boyer, 1993b). However, at high temperatures, the observations are reversed and peculiarly unexpected behaviour is observed in Ti-6Al-4V in the mill-annealed condition (see note 1 below) because of an interesting change in deformation mechanism leading to expectedly high ductilities resembling those of amorphous glasses rather than crystalline metals. The phenomenon is known as 'superplasticity' and most researchers attribute the mechanism of deformation to be one of grain rotation coupled with grain boundary sliding, with an inherent resistance to necking and thus to fracture, resulting in extremely high ductilities of the order of several thousand per cent in some materials, including this titanium alloy. It is the exploitation of this process that is described in this chapter for the manufacture of medical and dental devices and customised prostheses.

Note 1. The mill-annealed condition is a less controlled form of recrystallisation annealing which combines high fracture toughness, good hot formability and a high strength. For this condition, the material is heat treated in the $\alpha + \beta$ phase field and then recrystallised at subtransus temperatures. When the subsequent recrystallisation anneal is performed below the martensite start temperature, a fine microstructure consisting of α and β grains forms (Boyer, 1993a).

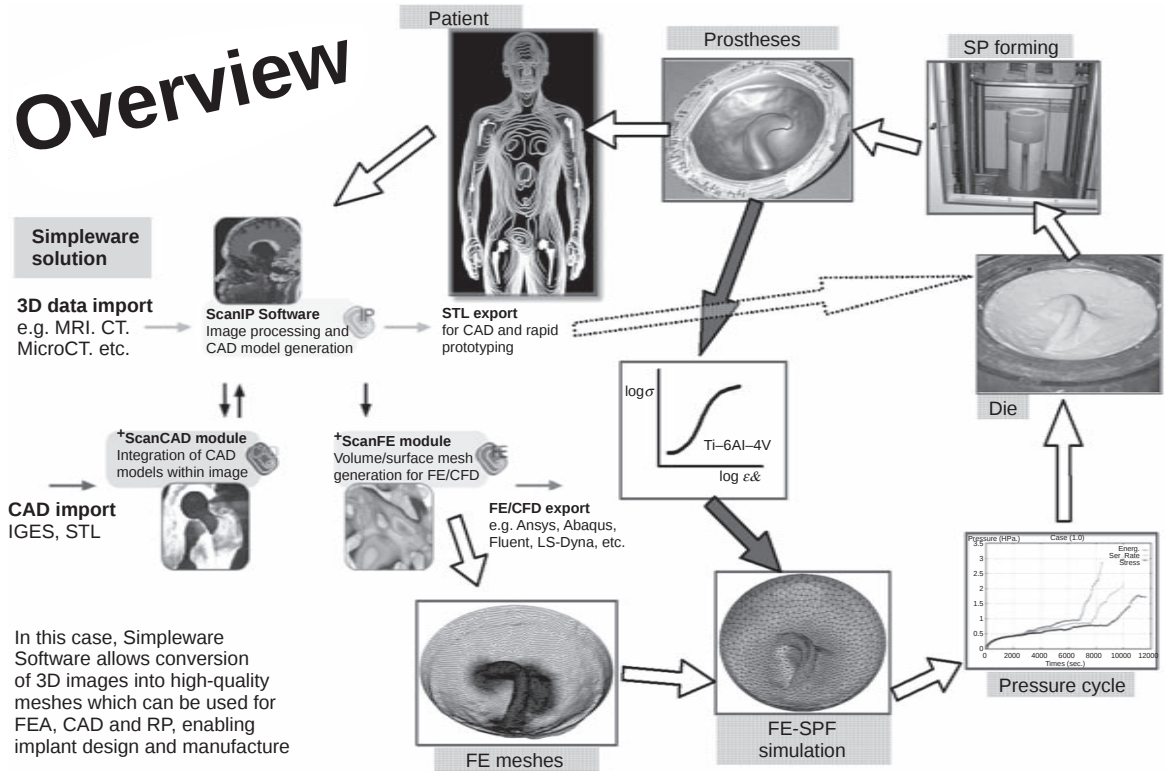
15.1.1 Mass customisation and customising prostheses

The customisation of prostheses has been growing decade by decade and, as with many products, the demand and the requirement for items that are unique to the individual is considerable. 'The medical field is one in which it could be argued there is a growing need for customisation, that will increasingly provide tailored devices and implants for unique physiologies, resulting in better overall treatment than the use of "off the shelf" devices and implants.' (Dalgarno *et al.*, 2006). Rather than being based on market forces associated with fashion, the need for customisation of medical devices and prostheses is arguably justified and in most cases customisation should lead to better performance and possibly to longer life of the implant. However, the customisation of implants is still in its infancy and currently means modularisation for certain types of implant, such as the total joint replacement. True customisation has not yet been attained. Designs and process developments leading to more cost-effective solutions are required which will allow prostheses such as these to be mass produced in shorter timescales (perhaps while the patient waits). Thus, the concept of mass customisation has been born and recently reviewed with reference to medical devices (Dalgarno *et al.*, 2006). This chapter dealing with the applications of superplastic forming (SPF) in medicine and dentistry is concerned, in part, with this issue.

The medical professions have for a long time used customisation at a craft based level in order to generate treatments and devices which are individual. In recent years more technological approaches to customisation have emerged within the medical arena, driven by advances in scanning technology, manufacturing technologies, and approaches to regenerative medicine. These advances have been in parallel with advances in computing technology which have allowed the data required to be communicated and analysed within a useful time scale (Dalgarno *et al.*, 2006).

These same advances in computer technology have also driven advances in computer modelling and simulation of the processes that may be used to manufacture prostheses.

One example of the use of computer technology to achieve customisation involves the use of the SPF process and the manufacture of dental and maxillofacial devices (Fig. 15.1). In this example, scanning techniques are used to image the region of interest in the patient once the injury has been stabilised. The scanning techniques may be laser scanning, to create a better fit to the outside of a patient, or MRI or CT scanning where information regarding the internal structure of the body is required. CT scanning is generally considered to be the more accurate approach for hard tissue, while MRI offers the better approach for soft tissue (Dalgarno *et al.*, 2006).



15.1 A schematic of the typical cycle for superplastic prosthetic forming in which the combination of imaging, computer modelling and rapid prototyping is used to manufacture an accurately fitting titanium alloy prosthesis for a patient. This can be done by incorporating the Simpleware software solution into the manufacturing cycle.

Computer software, such as SimplewareTM, can be used for different stages of the project to produce the customisable device. The modules that make up SimplewareTM can be described as follows. The ScanIP module is used for image processing and computer aided design (CAD) model generation; regions of interest from the scan can be isolated and even exported for CAD and rapid prototyping, an important step for die production. At the same time, the ScanFE module allows for volume and/or surface mesh generation and export to in-house or commercial finite element/computational fluid dynamics (FE/CFD) packages. In an FE/CFD package (the use of the FE-SPF SuperFlag[©] software solution is described in some detail in Section 15.3), the forming process itself can be simulated once sufficient material characterisation has been completed and suitable constitutive models that describe the material behaviour during large plastic deformation or flow have been developed. One further module in Simpleware, the ScanCAD module, also permits integration of CAD models with the CT/MRI/MicroCT image. ‘The assistance which is offered to surgeons from customised components is normally related to situations where some removal of tissue must occur in order to locate or secure an implant . . . The use of CAD tools can . . . be valuable in situations where the part of the body which is to be covered no longer exists (Tsuji *et al.*, 2004)’. For the manufacture of a facial prosthesis for a patient who had undergone surgery for cancer, the researchers had no geometric information for the side of the face for which the prosthesis was being manufactured, but after laser scanning, could, in CAD, mirror the other side of the patient’s face to create an appropriate prosthesis, which was then produced using CAD/CAM techniques (Dalgarno *et al.*, 2006).

The approach described in brief above using commercial software and metal forming is not entirely new. It has been foreseen by others that such an approach, which integrates support for the surgeon and the development of a device for long-term patient use, could be developed by the production of titanium plates for use in bone reconstruction, where the titanium plate would be customised to the implantation location (Pattijn *et al.*, 2002), (Wehmoller *et al.*, 2004). For this particular case, the approach, which had been based on CT imaging to determine the required geometry, and software for planning, used a layer manufacturing technique to create a mould against which the titanium plate could be formed. The titanium plate was intended for use after the removal of a tumour, and was expected to result in immediate stability and to aid in bone regeneration by acting as a stiff retainer for bone graft material held in a cavity created by removing the tumour. The bone graft material had been packed tightly into the defect before securing the outer titanium membrane, better facilitating the development of new bone. As the exact amount of material removed by the surgeon could not be known beforehand, the titanium plate was made

oversize, together with a Perspex replica of the titanium plate. In surgery, after the tumour had been removed the surgeon could use the transparent plate to assess how big the titanium plate needed to be for appropriate coverage, then the plate could be trimmed to size before attaching it to the outside of the bone (Pattijn *et al.*, 2002).

15.1.2 What is superplastic forming?

This brief introduction to the actual use of titanium membranes throughout the human body now leads us to consider how SPF might be useful in the production of similar prostheses and, furthermore, whether this process might have advantages over existing forming techniques, sometimes likened to auto-body forming methods. Before we consider in detail the SPF process itself, it is worth considering the nature of superplasticity.

Background to superplasticity and the unique characteristics of superplastically formable materials

Dealing now with the phenomenon of superplasticity, the term ‘parepisteme’ has recently been used in materials science (Cahn, 2001), referring to a subsidiary topic of research. Its literal meaning is a subsidiary domain of knowledge. Parepistemic research is not directly aimed at solving practical problems, even though industrial applications have arisen out of such work. In this context, it could be argued that the phenomenon of superplasticity might have been described as a parepisteme before mid 1970. Initially, the discovery of the superplastic phenomenon in metallic materials, which can be first traced back to Bengough in the early part of the twentieth century, was largely a scientific curiosity and it took more than half a century for a first patent to appear in 1970. Then, in 1976, the first major industrial advance was patented for SUPRAL 100 (Al–6wt% Cu–0.5wt% Zr) and was published in Britain (Grimes *et al.*, 1976). The superplastically formed material could be formed at reasonably fast strain rates and maintained its small grain size because of a fine dispersion of second-phase particles. Only modest stresses were required for forming; therefore, costly tool steels were not necessary. Currently, SPF is utilised in commercial production in the space, aeronautical, automotive, rail, architectural, sports and entertainment sectors, among others. Superplasticity has been shown to occur in many materials including ceramics and composites (Nieh *et al.*, 1997). Ductilities of the order of 1000–2000% are commonly observed in metallic superplastic materials although, commercially, elongations of 300% are usually sufficient to form even the most complex component geometries. The important features of a superplastic microstructure are fine grain size, stable microstructure, high-angle grain boundaries, grain

boundary diffusion and accommodation. Superplasticity is strain rate sensitive and typical forming rates are such that low to medium batch production is the norm, but that is now changing with the introduction of high strain rate superplastic materials and modifications in the technology resulting in similar forming techniques, such as Quick Plastic Forming™ developed by General Motors in the United States.

Applications in medicine and dentistry

With the developments that have been taking place in the last few years in microstructural refinement, leading to the production of small quantities of materials exhibiting high strain rates and superplastic elongations (Chandra, 2000), the SPF process is increasingly being applied to higher numbers in production runs and to other applications. Recently, the current authors and co-workers have been developing superplastic applications in dentistry and medicine. The driving force behind this work was initially the manufacture of dental implant superstructures using high-strength, mill-annealed titanium alloy (Curtis *et al.*, 2000). Since then, the range of applications has expanded and now encompasses: lower and upper complete and partial denture frameworks, implant-retained over dentures, cleft palate plates and hollowed-bulb obturators in dentistry, with further studies on maxillofacial applications such as skull plates for surgical repair of a defect or deformity of the skull (cranioplasty), superstructures for nose reconstruction and ridge augmentation membranes. Work also continues on the further development of customised fracture plates and augmentation devices such as malar augmentation and orbital floor reconstruction.

In contrast to the use of SPF, hot forming of titanium for implants is actually well documented and the benefits of using hot forming technology can be summarized as shown in the next section.

Benefits and guidelines for the hot forming of titanium for implants

- The best mechanical properties for metallic prostheses are achieved by forging.
- Both pure titanium as well as traditional $\alpha + \beta$ titanium alloys (Ti-6Al-4V and Ti-6Al-7Nb) can be forged into joint prosthesis components at temperatures between 900 and 950 °C.
- For hip prostheses, stem blanks are initially pre-heated in a furnace. The ensuing forming process in the slightly pre-heated dies (150–300 °C) causes the temperature of the forging blanks to drop rapidly and thus lose their good formability.
- In most cases it is necessary to achieve the final shape in several forging steps with intermediate heating up of the blanks.

- A more recent development based on the conventional forging technique is the so-called 'isothermal hot-die forging'; with this process, the dies are kept at the forging temperature (900–950°C, rather than at 150–300°C, as in conventional forging) by induction heating.
- Forming of the incandescent titanium blanks in the superplastic range can last as long as required, so that the material is able to flow into and around very complex die shapes with very small local radii without the necessity for intermediate re-heating.
- This process is particularly suitable for manufacturing complicated, thin-walled profiles without having to finish the work pieces using metal-cutting processes to net or near-net shape.
- Isothermal hot-die forging leads to uniformly textured structures, both in the less-deformed core region and also in the superplastically deformed regions of the alloy.

There are obvious advantages to isothermal hot-die forging as described above and these principles are most akin to fine-structure superplasticity (Nieh *et al.*, 1997) or the process of Superplastic Prosthetic Forming (a term coined by the authors) used for the manufacture of medical and dental prostheses. Other forms of superplastic deformation exist and include internal stress superplasticity and high strain rate superplasticity. Interestingly, commercially pure (CP) titanium lends itself more readily to hot deformation by internal stress superplasticity since the material exhibits an allotropic phase transformation at high temperature. If the material is thermally cycled through this phase transformation then higher ductilities can be achieved. However, the close-packed hexagonal α phase has fewer slip systems and a self-diffusivity that is approximately two orders of magnitude slower than that in the high-temperature body-centered cubic β phase. As a result, ductilities of only 100% have been observed in CP-Ti when deformed in this cyclic manner (Pilling and Ridley, 1988), and it is unlikely that this could truly be described as a superplastic deformation mechanism.

So, to move towards the development and commercialisation of fine-structure SPF of medical and dental prostheses, a press was commissioned to explore the technology in greater detail.

Equipment for superplastic forming of medical and dental prostheses

The designed press was a 20 tonne hydraulic press of the four-pillar, up-stroking type that is actuated by a precision screw jack with servo motor drive, with very accurate positional control for clamping the alloy sheet to create a gas seal. Induction heating is used to raise the temperature of a steel chamber and investment die insert to the forming temperature.

The die assembly (steel chamber plus ceramic die insert) is mounted on a ceramic insulating block and the induction coil with thermal insulation is mounted within the press frame. The induction coil is water cooled and is rated with a cold-start input power of 60kW and a maximum demand of 75kVA for heating the die assembly from room temperature to 900°C. It operates from a power supply of 415V, three-phase and 50Hz. The water passing through the closed circuit of the induction coil also passes through a heat exchanger. Chilled water at 10°C cools the water in the closed circuit to less than 25°C. The press is controlled by a programmable logic controller (plc) which itself is linked to a personal computer (pc). The plc is capable of running the press independently of the pc except for defining temperature set-points and pressure–time profiles. These are entered into the pc and downloaded to the plc and gas controller (in this case a Tescom unit – ER3000) before start-up. Once a die has been inserted into the steel chamber and the whole placed into the press, induction heating takes approximately 95min to reach the sheet insertion temperature, somewhere between 800 and 900°C. Temperature loss can be as little as 20°C when the press is opened to insert the titanium alloy sheet (140mm diameter and up to 3mm thickness). A low clamping pressure is applied at this stage to maintain argon gas flow above and below the forming sheet to protect against oxygen contamination. At the forming temperature, usually between 830 and 930°C, a clamping pressure of 6 tonne is applied, well within the 20-tonne capability of the machine, and gas pressure above the titanium sheet is raised in accordance with the pressure–time cycle. The pressure cycle runs automatically and consists of 32 pre-set data points. Between each pair of data points the pressure increases in a linear manner. On completion of the pressure cycle, the machine reverts to the lower clamping force until the temperature drops to the temperature for titanium sheet extraction, between 700 and 900°C.

15.2 Superplastic Prosthetic Forming – a process for the hot forming of titanium alloys for biomedical applications

15.2.1 Available materials and relationship to existing standards for implant surgery

It has already been explained that at high temperatures, peculiarly unexpected behaviour is observed in Ti–6Al–4V in the mill-annealed condition because of an interesting change in deformation mechanism leading to high ductilities resembling those of amorphous glasses rather than

crystalline metals. The phenomenon was described as superplasticity and most researchers attribute the mechanism of deformation to be one of grain rotation coupled with grain boundary sliding, with an inherent resistance to necking and thus to fracture. Such behaviour is characterised by high values of strain rate sensitivity index m , (>0.3); m , is the gradient of the log (flow stress) versus log (strain rate) relationship in the superplastic region – region II. Other titanium alloys (Pilling and Ridley, 1988) have also been shown to exhibit superplastic properties at specific strain rates and at temperature $>0.5T_m$ (T_m , melting point of the material). Experiments using the alloy SP700 will be described in Section 15.6.4 targeting maxillofacial applications.

Manufacturers of titanium alloys supplying material to medical device manufacturers must ensure that the materials conform to British and International standards for use as surgical alloys. The relevant British Standards for titanium alloys include: BS 7252-11:1995 for wrought titanium 6-aluminium 7-niobium alloy; BS 7252-10:1997 for wrought titanium 5-aluminium 2,5-iron alloy; and BS 7252-3:1997 for wrought titanium 6-aluminium 4-vanadium alloy. The standards call for specific requirements for mechanical properties and for composition. Some mill-annealed Ti-6Al-4V sheet products certainly meet the specification for both mechanical properties and composition in the as-received condition. The wrought Ti-6Al-7Nb alloy has also been shown to deform superplastically and has been described for use in medical implantation (Semlitsch *et al.*, 1992) and in biocompatibility studies (Spriano *et al.*, 2005) to assess *in vitro* behaviour as a prelude to implantation. Following similar studies, it is then up to the medical device manufacturer to show that the finished prosthesis is fit for purpose.

15.2.2 Requirements of a metal alloy for superplastic forming of medical and dental prostheses

The superplastically formed prosthesis should:

- (a) be manufactured from an alloy that meets the relevant international standard of alloys used for surgical implantation;
- (b) ideally, possess enhanced biocompatible properties after the hot (superplastic) forming operation;
- (c) fully adapt to the region of interest on the die surface;
- (d) be of sufficient thickness to allow for adaptation to the hard or soft tissue surface within the body, but should not deform under the in-service loads that may be applied to the prosthesis during normal bodily function;
- (e) be shown to be fit for purpose for the intended application;

- (f) not suffer from excessive loss of ductility due to pick-up of interstitials during the hot (superplastic) forming operation;
- (g) be cleaned in accordance with current practices relevant to the use of a medical grade alloy for the manufacture of prostheses, which will thus allow the prosthesis to integrate with hard and soft tissues in an appropriate manner;
- (h) ideally be cut from the formed sheet in an accurate and effective manner and/or finished accordingly, e.g. round edges using a form of barrel polishing.

15.3 Finite element modelling and superplastic forming simulation of SPF

15.3.1 What is a finite element-superplastic forming simulation?

Finite element simulation of superplastic forming (FE-SPF) is currently in use in industry and provides a useful virtual manufacturing environment where SPF components and the SPF process can be subject to investigation without the need for costly experimentation. In principle, for a given pressure cycle, FE-SPF simulation is able to predict the progress of forming through to complete or near complete contact with the die, giving the developing thickness distribution, grain size, equivalent flow stress and equivalent strain rate. Alternatively, for a given flow stress or strain rate, the simulation can provide an optimum pressure cycle. In this manner, FE-SPF can be considered as a virtual manufacturing environment within which SPF process ideas can be subject to investigation without the need for expensive practical experimentation.

15.3.2 Mathematical modelling

Modelling of the SPF process involves the mathematical representation of the physical forming process in terms of variables – for example, displacement or velocity. This modelling procedure must enshrine equations that fundamentally describe the process. Generally, these are the equilibrium, compatibility and constitutive equations. Equilibrium refers to the balance between the external pressure acting on the component and the internal stresses developed by the deformation or by the rate of deformation (in the SPF case). This balance is expressed as a differential equation relating external pressure and internal stresses. Compatibility implies a satisfaction of the boundary or support conditions together with equations that ensure physical continuity of the deformation. In general, this latter requirement is expressed as a differential

equation involving displacements. The relationship between the internal stresses and the strain produced by the deformation (or its rate) is provided by the so-called ‘constitutive equations’ (alternatively called a ‘material law’).

In order to develop the mathematical representation, it is almost inevitable that some approximations have to be made. These may involve restrictions, such as the geometrical description of the component and the manner in which it can deform, and almost certainly some approximations of the material behaviour (the constitutive equations). Having achieved a mathematical model of the real SPF process, it is now necessary to solve these equations in order to find the variables (velocity or displacement) that eventually provide the simulation of the real process.

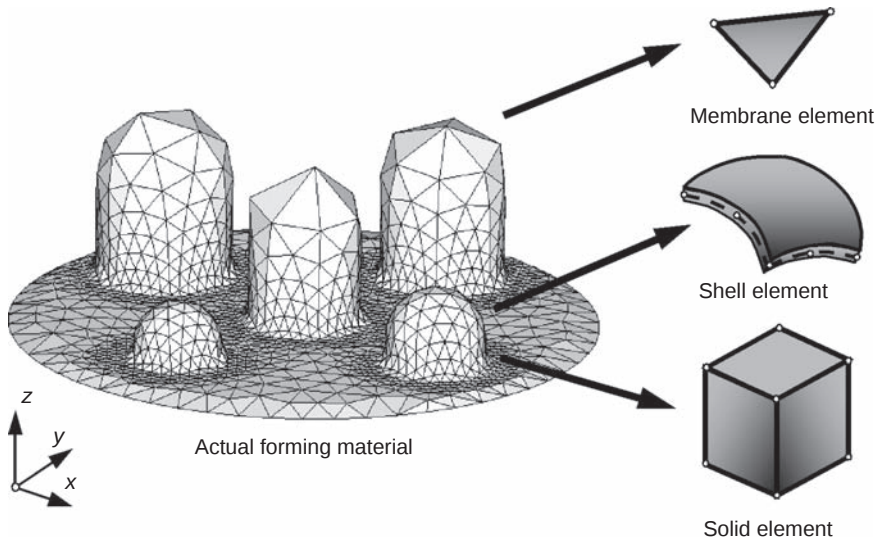
The solution of the mathematical model can be attained either analytically or numerically. Analytical solutions are confined to simple uniaxial or axisymmetrical situations such as bulge forming where an equation may be determined yielding an explicit relation between the input pressure and output velocities throughout the material. In the absence of an analytical solution, further approximations can be made to the mathematical model resulting in a so-called ‘numerical model’. These may be of a finite element or a non-finite element nature.

15.3.3 Numerical finite element modelling

In a finite element analysis, the continuous variables in the mathematical model are represented by a discrete set of variables. These discrete variables are located at so-called ‘nodes’, which define regions known as finite elements over which the variables can be simply interpolated. In this manner, the continuous problem is approximated. A collection of interconnected finite elements is called a ‘mesh’. If the variable itself is the position of a node, then the interpolation approximates the geometry of the region, see Fig. 15.2. Specifically, the velocity vector $\mathbf{v}(\mathbf{x}, t)$ can be interpolated throughout an element as follows:

$$\mathbf{v}(\mathbf{x}, t) = \sum_{a=1}^n N_a(\mathbf{x}) \mathbf{v}_a(t) \quad [15.1]$$

where: $N_a(\mathbf{x})$ is an interpolation function associated with node a in the element, known as a shape function; $\mathbf{x}$ is the position within the element where the velocity is required; while $\mathbf{v}_a(t)$ is the velocity vector at node a corresponding to time t . If the geometry and the variable fields are interpolated in the same way, the finite element is known as an isoparametric finite element.



15.2 Alternative finite element idealisations.

15.3.4 Superplastic forming simulation using finite element analysis

FE-SPF is an inelastic large deformation, incompressible (i.e. constant material volume) process and deformation-dependent pressure loading. In addition, the constitutive equations involve a non-linear viscous behaviour dependent upon an evolving grain size, the latter requiring an evolution law. Recall that a viscous material implies the relationship between the flow stress in the material and the strain rate developed as a result of the continuous deformation process. In so far as the flow stress depends upon the strain rate, the velocity of the deforming material emerges as the primary kinematic variable requiring solution. Alternatively, the velocity can be expressed in terms of displacement occurring over an increment in time. A kinematic description based on velocity is known as the ‘flow formulation’, while a description based on displacement is called the ‘incremental flow formulation’.

In order to make progress, it is now necessary to summarise the equations that emerge from an FE-SPF formulation. This enables the definition of several key variables required to characterise alternative approaches to the numerical solution. The finite element discretisation referred to above leads to a set of non-linear dynamic equations equivalent to Newton’s second law of motion relating mass M , acceleration a and force R , as:

$$R(v_{n+1}^k, x_{n+1}^k, t) = M(x_{n+1}^k) a_{n+1}^k \quad [15.2]$$

$$R(v_{n+1}^k, x_{n+1}^k, t) = T(v_{n+1}^k, x_{n+1}^k) - p(t)F(x_{n+1}) \quad [15.3]$$

The apparent simplicity of the above equations disguises the fact that they are a large set of non-linear simultaneous equations depending upon the number of nodes representing the forming material. Consequently, a , v and x contain the acceleration, velocity and position, respectively, of all nodes in the problem arranged in a column format. R represents the net effect of the internal forces, T , due to the internal stresses and the external forces, pF , where F is a set of nominal loads acting at the nodes and p is the pressure varying with time. Obviously, since R and a are column lists, M must be a matrix. Indeed, how M may be approximated or even included at all (since the material density is negligible in SPF) is reflected in the explicit and implicit solution schemes discussed below.

Irrespective of the solution scheme adopted the solution proceeds through time in a series of discrete time steps (i.e. from t_n to t_{n+1}), and depending on the particular solution technique an iterative scheme may be required where k indicates the iteration number.

15.3.5 Software/solution options

Simulation software, whether produced by individual research groups or by commercial companies, falls into two overall categories: that developed specifically for FE-SPF and that of a general nature suitable for a variety of viscoplastic (or creep) processes. In addition, as mentioned in the previous section, a further categorisation relates to the numerical solution scheme which may be either implicit or explicit.

Recognising that the density of the component is likely to be negligible, the mass matrix M can be omitted from equation [15.2], resulting in the quasi-static equilibrium equations given as:

$$R(v_{n+1}^k, x_{n+1}^k, t) = T(v_{n+1}^k, x_{n+1}^k) - p(t)F(x_{n+1}) = 0 \quad [15.4]$$

In an implicit solution the position, x_{n+1}^k , in equation [15.3] is related to the velocity as:

$$x_{n+1}^k = x_n + \Delta t v_{n+1}^k; \quad \Delta t = t_{n+1} - t_n \quad [15.5]$$

By substituting equation [15.5] into equation [15.4], the only unknowns in equation [15.4] now become v_{n+1}^k , the position x_{n+1}^k now being 'implied'. The well-known Newton–Raphson technique for solving non-linear equations is now employed to solve the above non-linear equations. Such an implicit scheme repeatedly involves the solution of a set of linear equations at each time step in the simulation in order to determine velocities and geometry that satisfy the quasi-static equilibrium equations. Generally a Newton–Raphson scheme involves iteration yielding increasingly accurate

approximations to the solution of the problem. For the problem under consideration this implies values of v_{n+1}^k and x_{n+1}^k that ensure that the quasi-static equilibrium equation [15.3] is satisfied within a specified tolerance. This is known as *convergence* towards a solution. This fundamental requirement can lead to occasional failure to achieve a solution and consequent overall failure of the simulation. The authors 'in-house' program Super-FLag© adopts an implicit approach.

Alternatively, in an explicit approach the mass matrix in equation [15.2] is retained and the forces calculated based on the previous time step t_n to give:

$$R(v_n, x_n, t) = M(x_n)a_{n+1} \quad [15.6]$$

Observe that the above equation is an approximation to equation [15.2] and consequently an explicit analysis is no guarantee of satisfaction of Newton's second law of motion. The simulation of the forming process can now be regarded as a dynamic analysis involving a time step by step calculation of the acceleration, a_{n+1} , from which the velocity can be updated as:

$$v_{n+1} = v_n + \Delta t a_{n+1}; \quad \Delta t = t_{n+1} - t_n \quad [15.7]$$

and the position updated using equation [15.5] omitting the iterative superscript k . Usually the mass matrix is approximated by having diagonal terms only and the acceleration can be calculated without the need to solve any system of linear equations. Such a procedure can be accurate and stable, and guaranteed to yield a solution provided that the time step is sufficiently small. This is directly proportional to the element size and the mass density, consequently a large number of small elements increases the computational time and artificial mass density has to be introduced to limit this problem.

While explicit dynamic simulation can avoid some of the convergence problems that may be experienced with the implicit approach, it is computationally time consuming due to the small time steps required for stability of the process. Even though an explicit scheme does not ensure satisfaction of the equations of motion, nevertheless a sufficiently small time step will provide a simulation of practical worth. Implicit solution schemes employ much larger time steps than explicit schemes and consequently can be computationally faster with the additional guarantee of the satisfaction of the equations of motion.

15.3.6 Constitutive equations

Superplastic constitutive equations are usually derived from uniaxial tests, or, more recently, from biaxial multi-dome tests. However, the simplest superplastic uniaxial constitutive equation is given by the Norton–Hoff

relationship between the equivalent flow stress, $\tilde{\sigma}$, and the equivalent strain rate, $\dot{\tilde{\epsilon}}$, as:

$$\tilde{\sigma} = K(g, T) \dot{\tilde{\epsilon}}^{m(g, T)}; m = \frac{\partial \ln \tilde{\sigma}}{\partial \ln \dot{\tilde{\epsilon}}} \quad [15.8]$$

where the viscosity K depends on the grain size g and the temperature T , and m is the strain rate sensitivity index whose value is crucial to the success of SPF. Accompanying this constitutive equation is a grain growth evolution equation which is expressed in terms of the sum of static and dynamic grain growth rates which are explicitly integrated as:

$$g_{t+\Delta t} = g_t + [\dot{g}_{\text{stat}}(g, T) + \dot{g}_{\text{dyn}}(\dot{\tilde{\epsilon}}, g, T)] \Delta t \quad [15.9]$$

A review of the literature reveals that there are many other superplastic constitutive equations of varying complexity.

15.3.7 Pressure cycle calculation

The success of SPF is strongly dependent on maintaining an optimal strain rate sensitivity index, m , which can only be achieved by varying the pressure with respect to time. Pressure cycle calculations employ a variety of formulations usually based on a maximum allowed desired target strain rate occurring anywhere in the forming material. Often, *ad hoc* rules are used to determine the pressure based on calculated ratios of actual to desired strain rate. The current authors prefer a more general algorithm whereby the rate of work done by the pressure is equated to the rate of energy dissipated in the forming material, which enables a direct calculation of the pressure evolution with respect to time. The rate of energy dissipated can be determined by targeting either the strain rate or the flow stress.

Assuming that the pressure cycle is unknown, an additional equation is required for its determination. This may be provided by constraining the average rate of energy dissipation per unit volume to match a target value e^0 . Since the rate of energy dissipation per unit volume is $\tilde{\sigma} \dot{\tilde{\epsilon}}$ the average can be easily found as:

$$e^0 = \frac{1}{v} \int_v \tilde{\sigma} \dot{\tilde{\epsilon}} dV \quad [15.10]$$

where v is the volume of the forming material excluding that in contact with the die. A number of alternative ways are available to calculate the target average rate of energy dissipation, for example weighting the actual strain rate $\dot{\tilde{\epsilon}}$ by a target flow stress $\tilde{\sigma}^0$ (i.e. replacing $\tilde{\sigma}$ by $\tilde{\sigma}^0$ in equation [15.10]) or weighting the actual flow stress $\tilde{\sigma}$ by a target strain rate $\dot{\tilde{\epsilon}}^0$; the latter is usually preferred in practice. In order to incorporate the target rate of

energy dissipation, e^0 , into the numerical scheme, it can be observed that e^0 is equal to the rate of work done by the pressure forces, that is:

$$e^0 = \frac{1}{v}(p\dot{V}) \quad \text{or} \quad p = \frac{e^0 v}{\dot{V}} \quad \text{where} \quad \dot{V} = \frac{V_{n+1} - V_n}{\Delta t} \quad [15.11]$$

and V is the volume of the gas enclosed within the forming sheet.

15.3.8 Idealisation issues

Idealisation is the way in which the deformation of the forming material is represented in the finite element formulation. It should be remembered that the analysis requires the division of the region of interest into an assemblage of finite elements. The shape of a finite element can vary from the simplest plane triangle to complex three-dimensional solid elements with curved boundaries. From a structural analysis perspective it is well known that the material can be idealised as a membrane, a shell or a solid. Membranes support the forming pressure by a uniform force (a stress resultant) only in the plane of the sheet. Shells support the load by an in-plane stress, which varies linearly in the thickness direction resulting in in-plane forces and bending moments. Neither include through-thickness stresses. Finally, solid elements include all six independent Cartesian stress components. The element employed in any particular analysis is largely dependent upon the ratio of the local thickness to radius of curvature occurring at any location and at any time during forming. It has been suggested that if the thickness is greater than one-sixth of the radius shell, solid elements should be used. Unfortunately, this is not known a priori: consequently, unless an estimate of the final thickness with respect to the smallest die radius can be made, experience is the only resolution. If membrane or shell elements are used, one layer represents the sheet, and triangles are usually better able to characterise the deformation. If solid elements are used, care needs to be exercised in the choice of element and the number used through the thickness direction. Figure 15.2 shows possible alternative idealisations of a forming sheet. Usually, elements of a different nature are not mixed in an FE-SPF analysis.

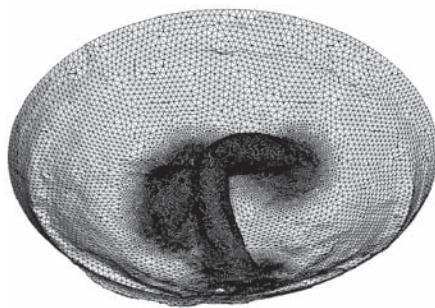
15.3.9 Meshing

Meshing means the way in which both the die and the forming material are represented in the analysis. Accurate and valid geometric definition of the die is the most challenging to achieve. Smooth semi-analytical NURBS modelling of the die surface can be employed. However, it is more useful to represent the die by a faceted surface mesh. The initial geometric definition is likely to be in the form of an IGES (or STL or OBJ) formatted file

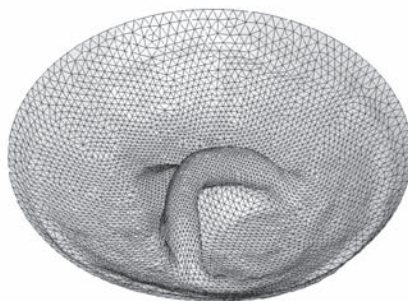
derived from some imaging technique. It is essential that the resulting surface definition is valid in the sense that the component surfaces are properly connected, that no overlapping occurs and that unintended holes do not exist.

If these problems can be overcome, many software packages are available to convert such geometrical definitions into faceted surface meshes of triangles and occasionally quadrilaterals. Again these meshes must be valid in that unique connectivity must pertain (corners must connect to corners), holes must not appear and normals to the surface must be in a consistent direction (say outward in the direction of the pressure); the latter requirement being crucial for pressure and contact calculations. In contrast to the mesh required for the discretisation of the forming material, the density of the die mesh can be considerably finer (see Fig. 15.3). Observe that the die mesh is simply a geometric representation of the die used to impose the boundary contact constraints and as such it is not an intrinsic part of the finite element formulation.

The mesh representing the forming sheet should be such that higher density meshes should be located in those areas anticipated to come into contact with die surfaces exhibiting complex detail. Since these cannot be predicted accurately, simulation software containing the potential for mesh refinement is desirable. The authors have employed this facility for membrane elements whereby mesh enrichment occurs when elements show excessive stretching or curvature based on average nodal information. Equally important is a procedure recently introduced by other investigators whereby pre-emptive mesh refinement occurs when a coarse mesh is near a die region having geometrical complexity incapable of being represented by the approaching mesh. Wherever possible, advantage should be taken of mesh-enrichment opportunities available in simulation software.



Example of die mesh



Example of formed sheet mesh

15.3 Contrasting die and sheet meshes.

15.3.10 Contact

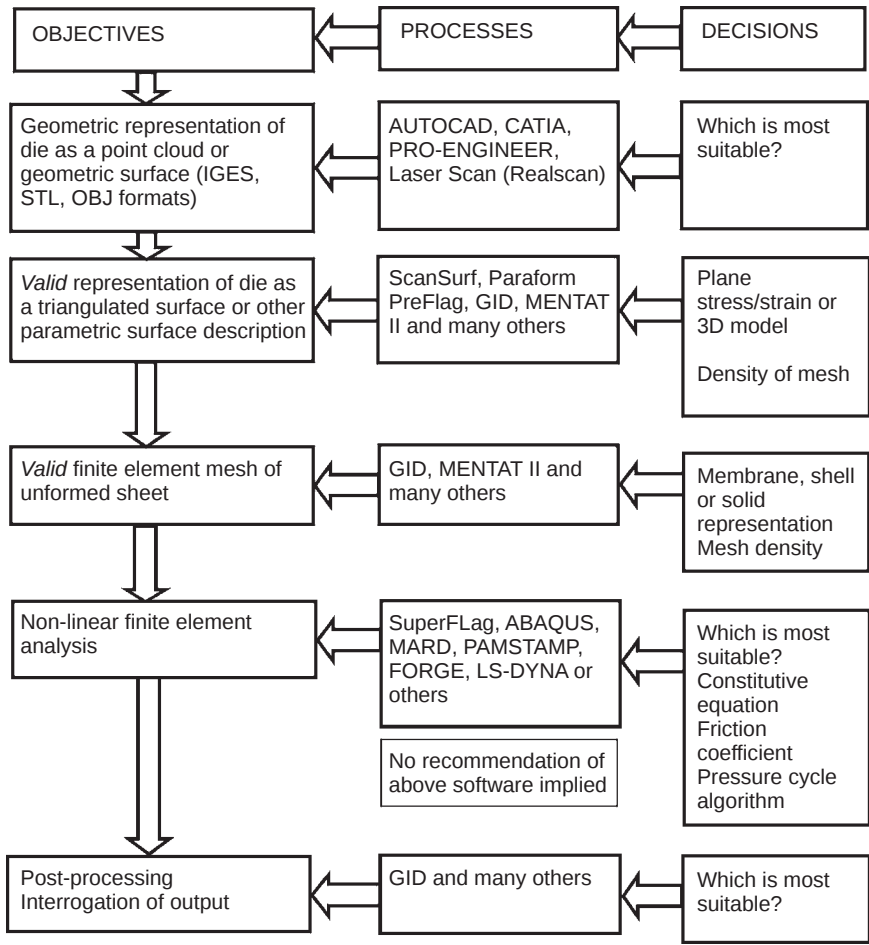
Contact refers to the numerical procedure by which it is ensured that the forming material remains on and does not penetrate the die. Inclusion of friction between the forming material and the die relates to those procedures that constrain the forming material to move tangentially to the die surface according to classical friction laws.

Inclusion of friction in the simulation of SPF is a challenge since coefficients of friction are largely unknown and indeed are likely to change during the process. In practice, valuable information may be obtained from simulations assuming complete sticking or sliding contact between the forming sheet and the die. However, sliding and frictional contact simulation is likely to be another source of convergence problems in implicit solution procedures. If, as is often the case, the die surface comprises flat-faced facets then the equations that are repeatedly solved in the Newton–Raphson iteration can change significantly as the node on the sheet moves from one facet to a neighbour with a different orientation. A myriad of techniques have been developed to alleviate the resulting convergence problems with considerable expertise being invested in commercial codes. The lack of strict adherence to the satisfaction of the laws of motion pertaining to an explicit analysis, enables contact and friction constraints to be more readily achieved.

15.3.11 Practical considerations

The success or failure of the SPF simulation using the finite element method is dependent upon many factors. These can be categorised into two groups: those independent of the finite element method and those dependent upon the finite element formulation and the accompanying solution procedures. In the former category can be included the constitutive equations and their characterisation, the friction conditions existing between sheet and die, the validity and geometric accuracy of the die description and the dimensions of the die in comparison with the thickness of the sheet. The latter category can include the element type used to represent the sheet (membrane, shell or solid), the material model employed (viscous flow or elasto-viscoplastic), choice of primary variables (velocities or displacements), formulation of sticking, sliding and frictional contact conditions, pressure control algorithm and method of solution of the non-linear equilibrium equations (explicit dynamic or implicit quasi-static), not all being mutually exclusive.

A guide to the many issues discussed above is summarised diagrammatically in Fig. 15.4. Ultimately, the success or failure of the simulation rests largely on whether the correlation between experiment and numerical



15.4 SPF simulation: practical issues.

output is acceptable throughout the progress of the forming. Only this will guarantee reliability of the finite element formulation and the accuracy of the constitutive equations. However, it may be the case that adequate qualitative information can be obtained even when strict compliance of the representation of the problem is relaxed.

Finally, it is important to emphasise that dental prostheses are unique to each patient, in contrast to mass production of industrial components. Consequently, the virtual manufacturing environment afforded by FE-SPF can be regarded as a valuable opportunity for the dental profession.

15.3.12 Simulation of a forming of a ridge augmentation membrane

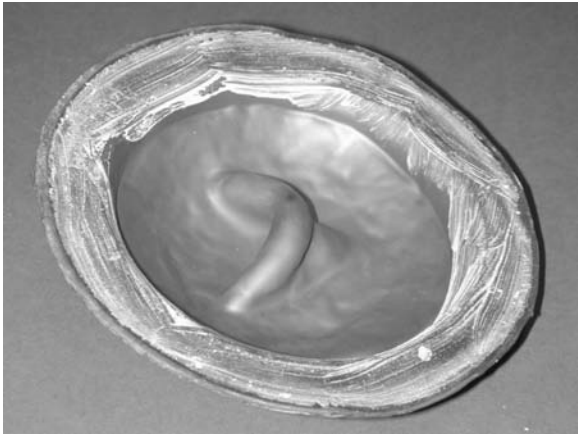
Ridge augmentation membranes (RAMs) are used in the rehabilitation of patients who have undergone extensive ablative surgery (cancers) or who have lost hard tissues from trauma. Implantation of this type of prosthesis comprises three major phases. The first is the initial fitting of the prosthesis to the bone surface which requires accurate matching of those areas on the prostheses that are attached to the patient. Once the prosthesis has been attached, then bone growth can be stimulated. This is achieved by osteo-promotion or by means of autogenous bone grafting using the iliac crest as a donor site. Within 15 months, the bone density below the titanium membrane is sufficient to be able to sustain the introduction of dental implants and restore function to the patient's jaws. Figure 15.5 shows the ceramic die and Fig. 15.6 a partially forming prosthesis.

Membrane element analysis

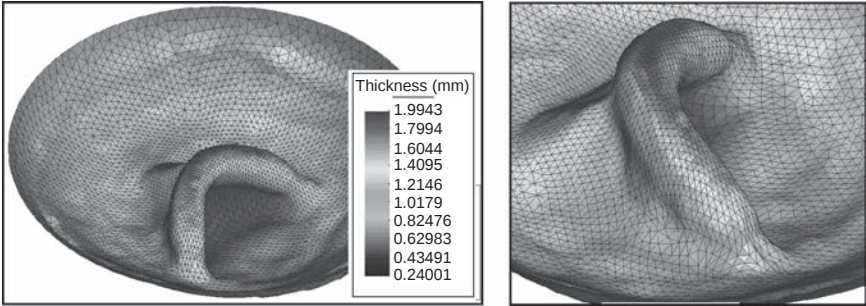
The initial sheet thickness is 2 mm, the radius is 55 mm and the target flow stress is 6.334 MPa. The RAM die comprises 54885 'elements' with 27561 points. For the simulation using three-node triangular membrane elements, the mesh comprised 10268 elements and 5198 nodes which increased to 10320 elements and 5224 nodes due to automatic mesh refinement. A predicted forming time of 9093 s was achieved in 158 increments, resulting in a maximum pressure of 2.48 MPa. Figure 15.7 shows the final thickness distribution. Observe that automatic mesh refinement is an important facility



15.5 Ridge augmentation membrane (RAM) ceramic die.



15.6 Ridge augmentation membrane (RAM) unfinished as formed sheet.

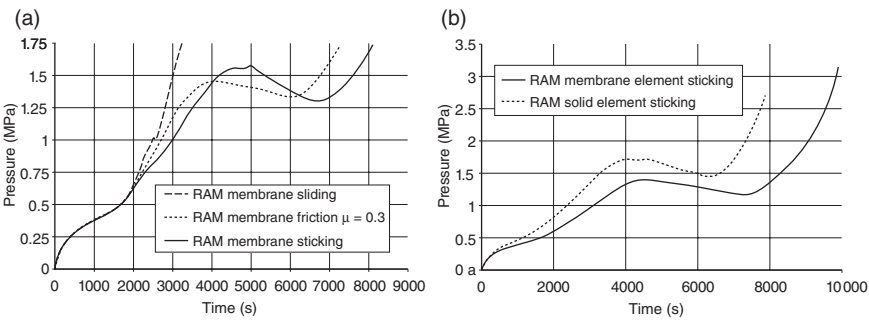


15.7 Ridge augmentation membrane (RAM) final thickness distribution.

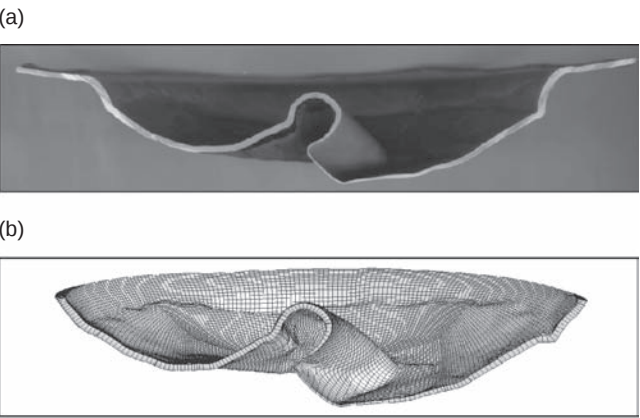
in that it enables an initially relatively coarse mesh to be automatically refined in those areas requiring increasingly higher geometric definition. Figure 15.8a shows the pressure cycles for various friction conditions between the sheet and the die. However, it should be noted that even an estimation of the friction coefficient is by no means trivial.

Solid element analysis

The analysis was repeated using 19200 solid eight-node elements with 38/722 nodes, and a predicted forming time of 22704s was achieved in 212 increments, resulting in a maximum pressure of 4.63 MPa. Figure 15.8b shows a comparison between pressure cycles predicted using the membrane



15.8 Ridge augmentation membrane (RAM), various pressure cycles.



15.9 Ridge augmentation membrane (RAM) comparison of thickness by: *a* experiment; and *b* solid analysis.

or solid element analyses. In so far as the single-layer solid element mesh accounts for bending behaviour in an over-stiff manner, it is to be expected that the solid element analysis requires a higher pressure profile.

Figure 15.9 shows a comparison between experimental and solid analysis thickness along a section of the die (see Fig. 15.5). The analysis reveals that grain size in the undercut region has increased from an initial value of $5\text{ }\mu\text{m}$ to approximately $11\text{ }\mu\text{m}$.

15.4 Geometrical modelling and superplastic forming simulation

To continue the theme of SPF modelling by computer simulation, an alternative approach to the finite element method has been developed which is based solely on the geometry of the die.

15.4.1 Why adopt a geometrical approach to modelling?

The prediction of final thickness is always a crucial issue during the design stage of an SPF component, partly because a difficult compromise exists between the mechanical strength of the component and its weight. The most important factor controlling the final thickness of the component is the geometry of the surface of the tool. The average of the final thickness is, for instance, equal to the ratio between the initial volume of the sheet and the area of the tool surface. However, under usual industrial conditions, uniform thickness is rarely achieved, so an understanding of the thinning process becomes decisive. Other parameters like the pressure cycle, the superplastic properties and the lubrication have less influence, to the first degree of approximation. The initial thickness of the sheet is certainly also critical, but its influence on the final thickness distribution is absolute, not relative.

During forming, the superplastic sheet has to adjust its shape under at least four constraints: the clamping boundary conditions, the gas pressure on one surface, the reaction of the die on the other surface and its own internal stresses due to deformation. Numerical simulations like the finite element methods described above, have made tremendous progress during recent decades in accurately modelling these interactions (Wood and Bonet, 1996). Although the determination of optimised pressure cycles and the use of advanced constitutive models for superplasticity have now reached maturity, the sheet–die interactions are often a source of difficulties. The contact formulation may also reduce considerably the speed of numerical simulation. This is partly due to the fact that contact is evaluated without considering the global geometric relations between the die surface and the sheet. In addition, criteria for adaptive meshing usually do not take into account the geometric properties of the die.

On the other hand, geometric approaches to SPF have regularly provided useful numerical methods to simulate the process. Although these methods generally make rough assumptions about the mechanical behaviour, their results may be sufficiently accurate and rapid to provide useful parameter optimisations of the process. The geometrical methods, however, are not easily applied to truly non-symmetrical, three-dimensional problems and are usually restricted to axisymmetrical or plane strain situations. What are the reasons that make the ‘jump’ from two-dimensional to three-dimensional so difficult?

Firstly, the problem is transferred from mechanics to geometry by making a radical but intuitive assumption: the superplastic sheet behaves like a soap bubble. By doing this, many important aspects of SPF are deliberately ignored. After considering the shape of a soap film bounded by a given curve, the effect of applying a differential pressure on one

of the surfaces is studied. Then, the rigid surface of the mould is introduced to present a new way of looking at the contact formulation. Finally, the two-dimensional case is exposed with practical applications in superplasticity and then ideas for the exploration of the general three-dimensional case are proposed.

15.4.2 Soap films and their shape

At the interface between a liquid and air, the fluid molecules are on average pulled into the fluid due to electrical forces. This phenomenon produces the so-called ‘surface tension’ in the region of the interface. As a soap film consists of two such interfaces with a thin layer of fluid between them, it will naturally tend to minimise its surface area (and more generally its potential energy). In 1760, after L. Euler, J. L. Lagrange established the important relationship between the minimal area condition and the shape of the surface, i.e. the mean curvature H at each point of a minimal surface is zero:

$$\text{Minimal surface: } H = 0$$

Several famous mathematicians such as K. F. Gauss and M. S. Germain have contributed to a better understanding of the concept of surface curvature. Then, in the middle of the nineteenth century, after many soap film experiments, a Belgian physicist, J. Plateau, set the famous Plateau’s problem:

Given a curve Γ , find a minimal surface M having Γ as boundary

This difficult problem was only solved a century later, and independently by several mathematicians, namely Garnier (1928), Radò (1930) and Douglas (1931). Even the father of the finite element method, R. Courant, was also involved in the study of minimal surfaces and their physical counterparts: the soap films. More recently minimal surfaces have found remarkable applications in architecture, for example, the Olympic Stadium in Munich. The German architect Frei Otto actually used soap models with mechanical loading during the design stages of the project. Introductory literature about the mathematical study of soap films can be found elsewhere (Hildebrandt and Tromba, 1985; Berest, 1997; O’Neill, 1997; Oprea, 2000).

15.4.3 Incorporating pressure in the analysis

When a differential pressure is applied to one side of a soap film, the newly born soap bubble adopts a different shape. Due to the surface tension, the soap bubble still tends to minimise its surface area, but this time under volume constraint. The relationship between the differential pressure and

the shape of the soap bubble was established circa 1800 by P. S. Laplace and T. Young and is simply:

$$p = 2H\tau \quad [15.12]$$

where p is the differential pressure and τ is the surface tension. In other words, at each point of a soap bubble, the mean curvature is constant. This leads to a new family of surfaces: the constant mean curvature surfaces or CMC surfaces.

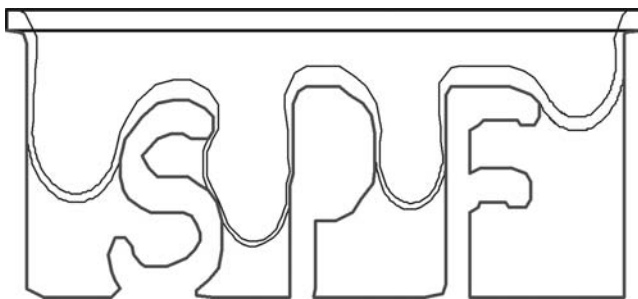
$$\text{CMC surfaces: } H = H_0$$

During the past decade, the study of CMC surfaces has become an active branch of mathematical research thanks to the continual improvements of computer graphics. Also, there are now a number of methods available to compute CMC surfaces numerically, but mathematicians have devoted their efforts mainly to the construction of abstract surfaces (infinite periodic, etc.) rather than to specific physical situations. Nevertheless, the generalisation of Plateau's problem, when the differential pressure is different from zero, is now:

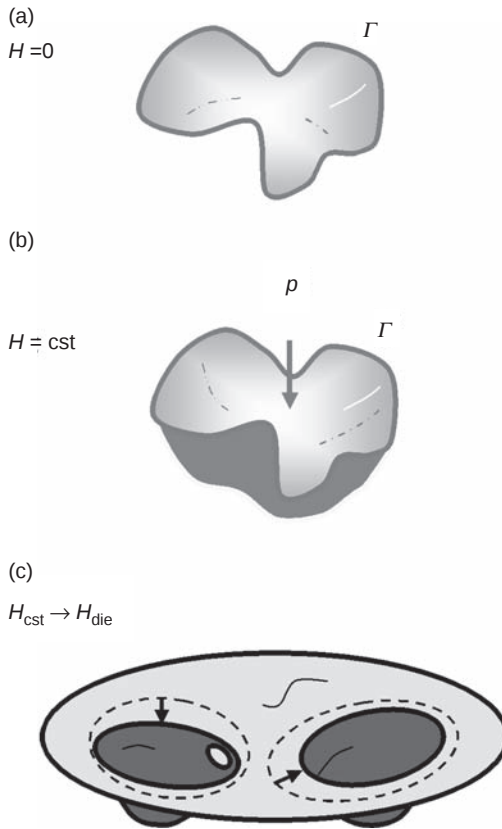
Given a curve Γ , find a CMC surface M having Γ as boundary and H as mean curvature

15.4.4 Introducing the die surface into the analysis

Obviously, the principal aim of SPF in technological applications is to manufacture components of prescribed geometry. So, the introduction of the die into the process will lead to a sort of 'curvature contest', i.e. a competition between the natural tendency of the superplastic sheet to minimise its area, and the obstacle presented by the shape of the tool (Fig. 15.10). A recapitulation of the SPF process from the curvature point of view is presented in Fig. 15.11. As the superplastic sheet progresses under the influence



15.10 The curvature contest during superplastic forming.

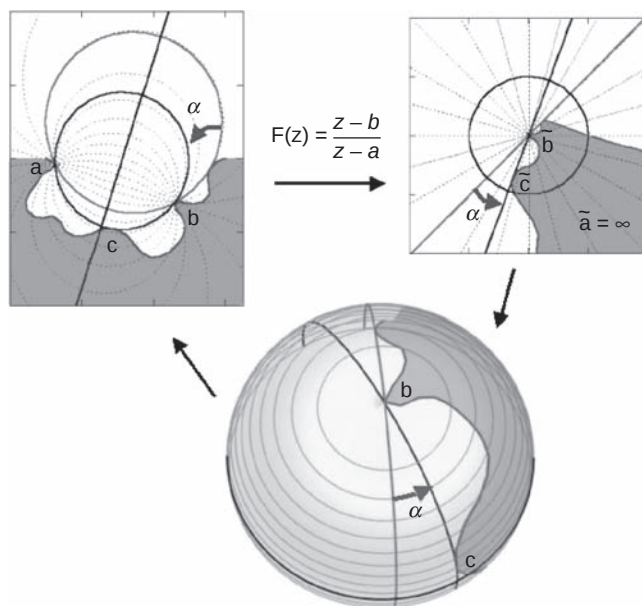


15.11 The three stages of superplastic forming from the curvature point of view: *a* clamping without pressure, the sheet is a minimal surface; *b* free forming, the sheet is a surface of constant mean curvature; *c* contact with the tool, the sheet progressively adopts the curvature of the die.

of the forming pressure, the area of contact with the die increases, and the Γ boundary curves of the free bulges are altered. Unfortunately, this complex evolution is not readily predictable in the general case.

15.4.5 Use of the Möbius transformation

In order to simplify the situation, we can start to examine the two-dimensional case. CMC surfaces become simply circular arcs, and the Γ boundary curves are reduced to pairs of points. The contact formulation is better illustrated by the help of elliptic Möbius transformations (Fig. 15.12), where one of the contact points (b) is mapped to the origin and the other



15.12 The two-dimensional contact algorithm is greatly simplified by mapping the plane R^2 to itself with an elliptic Möbius transformation or by immersing the problem onto the sphere S^2 in R^3 .

(a) to infinity (Needham, 1997). After mapping the plane to itself with this transformation, the forming sheet becomes simply a line rotating about the origin. This method allows us to find the next contact point (c) directly, without having to check the whole die surface. Another interesting way to visualise this process is to map the plane onto the sphere in three-dimensional space. Now, the contact points are mapped to the poles of the sphere and the forming sheet becomes half a meridian revolving about the pole axis. As so often happens in physics and mathematics, this type of immersion facilitates the resolution of a rather difficult problem in the original space. Recently, this methodology has been successfully applied to the SPF of dental prostheses.

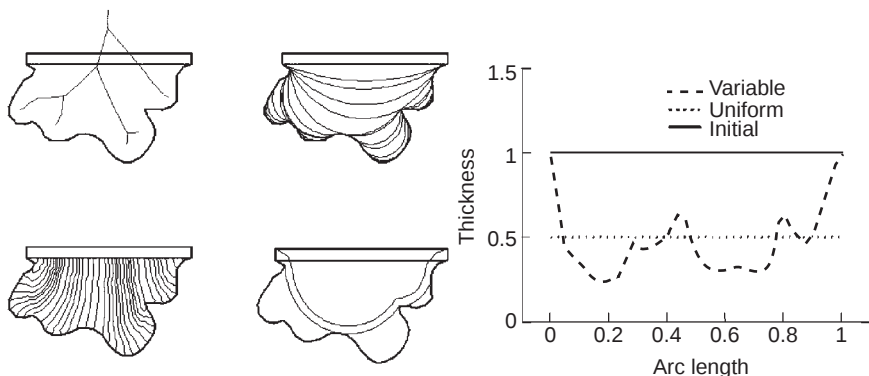
15.4.6 Implementing the geometrical approach

A form of modelling of SPF quite distinct from FE-SPF and using a solely geometrical approach has been developed and is based on a

condition of plane strain and using complex number analysis (Garriga-Majo and Curtis, 2001). Firstly, the cross-section of a stone model is scanned on a flat-bed scanner. The resulting image is interrogated by grey-level scale to determine the surface contour. A predetermined number of points are chosen to represent this surface. These points representing the die surface are then used in software, known as 'Multiform', to simulate the adaptation of the sheet. Before running Multiform, the flow characteristics of the sheet must have been determined. Multiform generates a gas pressure cycle by determining the pressure that will bring the deforming sheet, represented by arcs, into contact with the die surface at some new point – arc a–b reaching point c in Fig. 15.12 (NB The arc length depends on the number of points chosen to represent the titanium sheet). This approach currently assumes sticking contact. Complex number analysis is applied by associating a complex number to each point on the contact curve. In this way, intrinsic features of the contact curve, such as arc length between two points and total arc length, can be evaluated. The information that is derived about the surface and its contour is later used to assess the fit (Fig. 15.13).

15.4.7 From three dimensions to four dimensions

Surprisingly, immersion again could help to resolve the complex general situation, for CMC surfaces in three dimensions to become minimal surfaces onto S^3 , the unit 'sphere' in four dimensions. The generalisation of the elliptic Möbius transformation to predict the new contact points with the die surface, however, is not straightforward, and would necessitate further



15.13 Determination of the final thickness profile by using the two-dimensional contact formulation in the geometric analysis of superplastic forming.

investigations. This would also require working with quaternions instead of complex numbers to manipulate geometric entities in four dimensions. Monitoring the Γ boundary curves would also certainly require special care in order to correctly follow the generation, the splitting and the coalescence of these curves throughout the specific forming operation.

15.4.8 A final perspective on geometrical modelling

Many aspects of the SPF have been deliberately ignored in this brief exploration into non-finite element methods of modelling in order to emphasise the geometric aspect of the process. Starting from soap films and minimal surfaces it has been shown that the superplastic sheet could be represented by surfaces of constant mean curvature, to the first degree of approximation. An efficient contact formulation has been presented for the two-dimensional case but requires generalisation to the three-dimensional situation. Nevertheless, it could be possible to bring the soap bubble back into finite element methods in the near future, by introducing a new type of element: the CMC element (Γ, H) for instance. Finally, a better knowledge of the geometry of SPF is always beneficial. Anticipation of the shape of the superplastic sheet, especially during the final stage of the process, could lead to a better optimisation of the tooling design process. With the actual progress in computer graphics, it is now easier to design shapes with geometrical constraints such as surface curvatures, and we could envisage a new type of modelling coming into existence, known as 'geometrically enhanced SPF tooling'.

15.5 Ceramic die materials for superplastic forming in dentistry and medicine

A significant benefit of forming maxillofacial prostheses from titanium sheet is the biocompatibility of the metal surface which consists of TiO_2 . Recent studies have shown that fluoride modification can enhance the rate of osseointegration of dental implants and also the level of bone support (OsseoSpeedTM). We have already indicated that for maxillofacial prostheses the approach adopted is usually to cold form commercially pure titanium under relatively high levels of load and for considerable periods of time to overcome the springback that occurs. Splitting of the sheet is often expected, depending on the shape being formed, requiring judicious positioning of the key features of the prosthesis in the die. Dies used for these cold forming operations may be based on layered paper sheet structures or even various gysum products.

On the other hand, the ideal requirements of a die material for SPF are quite specific and in some cases different from those demanded above. The perceived ideal requirements of an SPF die material for applications in medicine and dentistry are listed below.

15.5.1 Requirements of a die material for applications of superplastic forming in medicine and dentistry

The die for SPF of medical and dental prostheses should:

- (a) have sufficient strength and durability to resist hot creep deformation;
- (b) harden and set in a reasonable time scale to be used in accordance with current dental and maxillofacial laboratory procedures;
- (c) have excellent sag resistance under its own weight at high temperatures and under the pressures of the forming metal sheet;
- (d) exhibit resistance to crack initiation and/or propagation either inherently or through the design of physical features incorporated into the tool that prevents crack propagation into the region of interest;
- (e) where necessary, allow for re-entrant surfaces to be incorporated into the die;
- (f) be strong in compression to resist hot deformation and accompanying loss of accuracy of the prosthesis;
- (g) be relatively weak in tension to allow the fully adapted sheet to be removed from the die surface if there are re-entrant (undercut) surfaces present in the die;
- (h) expand and contract in a reproducible manner;
- (i) allow for appropriate dimensional compensation of the forming sheet resulting from a mismatch in thermal properties between the metal sheet and the die material;
- (j) allow for accurate reproduction of surface features of hard and soft tissues;
- (k) enhance the biocompatibility of the formed prosthesis rather than cause a loss of potency for direct bone or soft tissue integration;
- (l) be easy to handle and cost effective.

The strength of dental investment casting materials and their resistance to hot deformation will not be dealt with here. Studies have been carried out to attempt to measure these properties and the reader is referred elsewhere (Juszczyk *et al.*, 2000, 2002, 2007). The remainder of this chapter will be concerned with examples of SPF prostheses, highlighting the need for compatibility between the thermal properties of the forming metal sheet and the investment die materials, and the need for biocompatibility of the as-formed titanium alloy surfaces.

15.6 Dental implant superstructures and surgical repair of a defect or deformity of the skull (cranioplasty)

In order to illustrate the key properties required of a die for Superplastic Prosthetic Forming, we now describe the use of SPF to produce two types of prosthesis; namely, a dental implant superstructure and a titanium alloy cranioplasty. A range of titanium alloys could potentially be used to form maxillofacial prostheses, but in these examples the alloys used are Ti–6Al–4V and Ti–4.5Al–3V–2Fe–2Mo (SP700) and the materials used for the die are commercial dental casting investment materials.

Finite element modelling using the SuperFlag® FE-SPF program (already described in some detail in previous sections) was used to simulate SPF and to calculate the argon gas pressure profiles required for SPF following the FE-SPF theory and methods described earlier. Temperature can be used as a variable to assess the relative importance of the thermal properties of the sheet and die materials, and their compatibility; more specifically, that similar ranges of expansion are obtained on heating to the forming temperatures (Soo *et al.*, 2001, 2004). Using this approach, accurate prostheses have been formed at King's College London using the SPF technique and dimensional tolerances measured using contacting scanning surface mapping techniques.

15.6.1 The requirement for accurate fit

Typically, the forming of dental and maxillofacial prostheses relies upon the use of traditional techniques such as lost-wax casting for crowns, bridges, partial denture frameworks and implant superstructures, and a simple cold forming technique for maxillofacial prostheses such as cranioplasties and other skull defects. These techniques are reasonably successful at achieving the desired complex shapes of such components; however, with the developments that have occurred in implant dentistry and the demand for metallic prostheses in areas such as the zygomatic arch where in 100% of cases implants fitted in the area could not be fitted without an initial gap (Wehmoller *et al.*, 2004), it has become apparent that more accurate forming techniques are required for some customised implants.

In dental restorative treatment, probably the most accurate fit is required for implant superstructures. The fit is particularly important because tolerances outside $\pm 30\mu\text{m}$, considered by many to be the clinically acceptable fit, may contribute significantly to mechanical failure of one of the components in a reconstruction. An implant superstructure is described as that part of the prosthesis that is attached to the transmucosal elements of the implants and onto which the replacement prosthetic teeth are constructed

(Fig. 15.14). The superstructure is usually made out of metal and can be screwed or cemented in position.

The function of the superstructure is to provide a base onto which the missing tissues are constructed. It is attached to the implant fixtures via the transmucosal element of the implant system. In addition to this, the superstructure must have sufficient strength to withstand masticatory forces, be of a shape that is in harmony with the oral cavity, and fit accurately and passively.

The dimensions of superstructure frameworks have largely been determined by anatomical constraints, available space and factors associated with the mechanical properties of the alloys used in their construction. They are also dependent on the number, length and distribution of implants.

The design of the prosthesis and implant position has a significant influence on the bone stress in addition to the stress on the screws, and these factors are especially important when designing any cantilever portion of the framework. Often it is not possible to construct a framework to 'ideal dimensions' since they are custom-made and other factors may take precedence in their design. The resulting restoration may already be compromised and could show a reduced lifespan. The 'ideal dimensions', considering all factors, need to be determined in each case.

The purpose of a cranioplasty, on the other hand, is to achieve morphological and functional rehabilitation of the cranial vault affected with a severe bony defect resulting from trauma, infection, tumour or a cerebral decompression procedure. A cranioplasty may be required to replace up to three-quarters of the surface area of the calvarium, and can be fashioned from titanium mesh or plate. The requirements of a cranioplasty are that



15.14 Implant-supported superstructure.

the material should be inert or biocompatible, non-thermal conducting, radio-transparent, non-magnetic, lightweight, possess appropriate physical and mechanical properties, and be economically viable.

Therefore, specifically, it is necessary to establish the optimum expansion of a number of dental casting investments for use in the SPF of titanium alloys to successfully form titanium dental implant superstructures and cranioplasties.

15.6.2 Investigating appropriate combinations of titanium sheet and investment die materials

In order to find appropriate combinations of alloys and investment die materials to form implant superstructures and cranioplasties, models for SPF have been made using different types of dental casting investment materials and different special liquid proportions. In the following sections, we describe the investigation of these materials and combinations.

15.6.3 Dental implant superstructures by superplastic forming

A steel master model was constructed to incorporate two stainless steel implant abutment analogues (DCB-175, Nobel Biocare, Göteborg, Sweden) with their centres 8mm apart. Two holes were drilled into the baseplate and the abutment replicas were secured into the baseplate with resin adhesive (Quick Set Epoxy Adhesive, RS Components, Corby, UK). A plastic beam that measured 50 mm × 10 mm × 4 mm was made. Two holes were countersunk into the undersurface of the beam so that they fitted over the abutments of the master model, then resin adhesive was put into the holes and the beam placed onto the abutments so that when set the plastic beam could be removed and replaced back over the abutments.

The plastic beam was used as a transfer jig to 'pick-up' two Nobel Biocare abutment analogues (DCB-175, Nobel Biocare, Göteborg, Sweden) in the holes of the undersurface, thus eliminating the need for an impression when transferring the position of the abutments via an impression coping. The undersurface of the plastic beam was lightly coated with petroleum jelly (Vaseline, Chesebrough-Ponds Ltd, London, UK) to act as a separator. For each model, 100 g of dental casting investment were weighed and three different proportions of special liquid and water (Table 15.1) were measured with a 25 cm³ pipette (Technico Pipette, London, UK) then hand mixed with the powder for 60s and vibrated for 30s (Vibrating Platform, Castellano, Torino, Italy). For the DM/D investments three powder ratios of DM

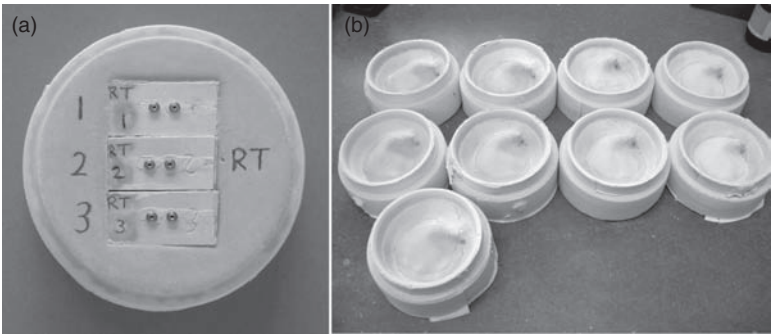
powder and D powder were used. The investment mixture was poured into a rubber mould and the plastic beam with the abutment analogues inverted into the investment. This was allowed to set at room temperature for 1 h (2h for DM/D investment), after which the plastic beam was removed leaving the abutment analogues embedded in the investment.

A Perspex[®] mould, the same size as the heat-resistant ring that holds the SPF die and goes inside the die chamber of the in-house SPF machine, was lined with wetted casting ring liner (ceramic fibre casting ring liner, Bracon Ltd, Etchingham, East Sussex, UK). Then 1 kg of Croform WB dental casting investment (Davis Schottlander and Davis, Letchworth, Hertfordshire, UK) was weighed and hand-mixed with 137 ml of water. The mixture was poured into the mould and three investment models (one of each special liquid or powder proportion) were pushed into the wet investment ensuring they were at the same level. This was allowed to set for 1 h before removal from the mould (Fig. 15.15a) and insertion into the heat-resistant steel SPF ring. The die was then left for 2 days before forming following the schedule for SPF.

Table 15.1 Investments and liquid or powder ratios used to make SPF models

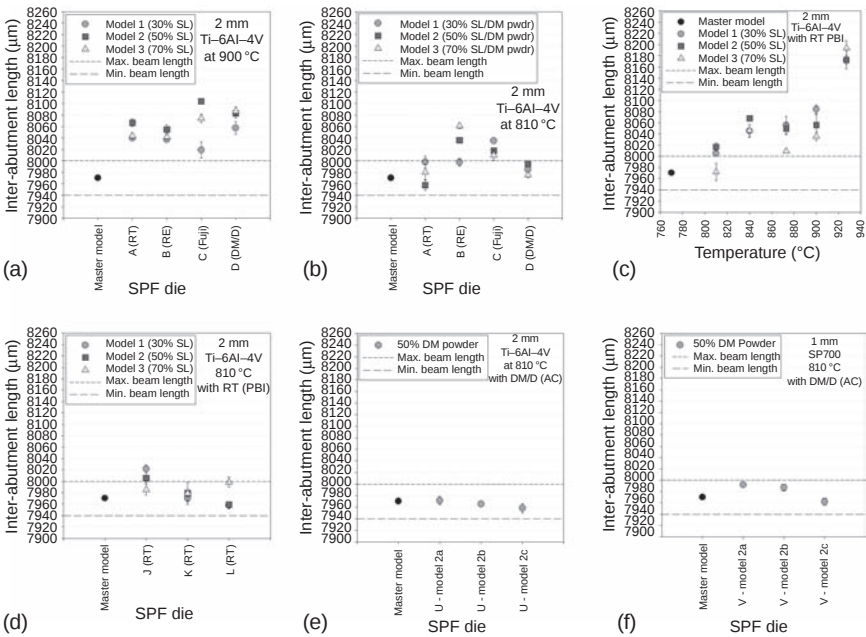
Investment materials	Powder (g)	Model 1 (30% special liquid/30% DM powder	Model 2 (50% special liquid/50% DM powder	Model 3 (70% special liquid/70% DM powder
RT	100	4.8 ml	8.0 ml	11.2 ml
RE	100	4.8 ml	8.0 ml	11.2 ml
Fuji	100	6.6 ml	11.0 ml	15.4 ml
DM/D	100	30 g (17.7 ml H ₂ O)	50 g (17.5 ml H ₂ O)	70 g (17.2 ml H ₂ O)

RT: Rematitan; RE: Rema-Exact; Fuji: Fujivest super; DM/D: types of Selevest Investment.



15.15 a SPF die containing three investment models representing the position of two dental implant abutment heads and *b* SPF dies for forming cranioplasties.

The degree of fit, as measured in two dimensions of the SPF formed titanium beams (representing implant superstructures), onto the implant abutment master model as a function of investment material, water to power ratio and temperature is shown in Fig. 15.16. Figure 15.16a shows that all investments selected have clinically unacceptable fit using Ti-6Al-4V alloy at 900 °C. Apparently 30% special liquid improves fit compared with other special liquid ratios. In Fig. 15.16b a marginal improvement in fit is observed when forming Ti-6Al-4V at 810 °C, although in some cases the fit is still clinically unacceptable. In Fig. 15.16c the Ti-6Al-4V alloy shows improving fit as the forming temperature is reduced from 900 to 810 °C and Fig. 15.16d confirms that at 810 °C the fit is consistently maintained for more than one die model of RT investment. The same result is observed for Ti-6Al-4V alloy on DM/D investment at 810 °C. When the SP700 alloy is used in place of Ti-6Al-4V alloy at 810 °C on DM/D investment a clinically acceptable fit is also achieved.



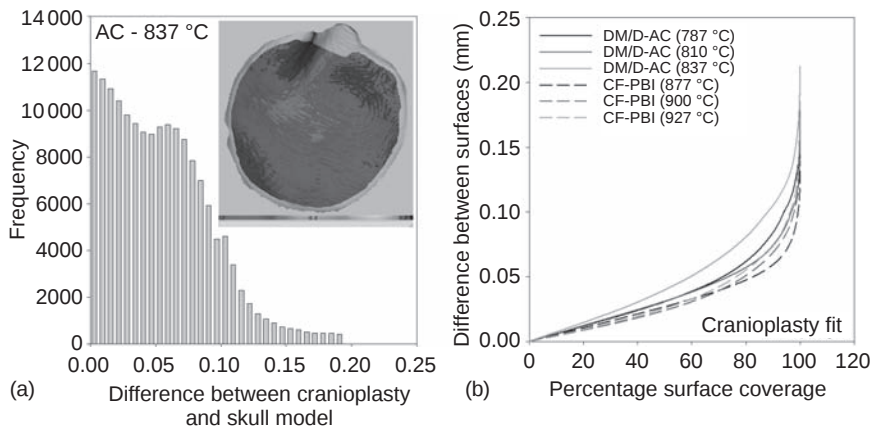
15.16 Fit of SPF titanium alloy sheet onto master model representing two implant abutments: (a) 2 mm Ti-6Al-4V sheet at 900 °C; (b) 2 mm Ti-6Al-4V sheet at 810 °C (c) 2 mm Ti-6Al-4V sheet with RT phosphate-bonded investment (PBI) die material; (d) 2 mm Ti-6Al-4V sheet at 810 °C with RT phosphate-bonded investment die material; (e) 2 mm Ti-6Al-4V sheet at 810 °C with DM/D aluminous cement (AC) investment die material; (f) 1 mm Sp700 sheet at 810 °C with DM/D aluminous cement investment die material.

This study has shown that clinically acceptable fits can be obtained when forming implant superstructures using the SPF technique and low-cost die materials made from dental casting investments. Both Ti-6Al-4V alloy and SP700 can be formed at lower temperatures of 810°C to achieve this fit. However, practically, the SP700 alloy would be preferred since the flow stresses of the Ti-6Al-4V alloy are far too high at this temperature and the alloy is outside its SPF regime. SP700 alloy at 810°C on the other hand exhibits similar flow stresses to Ti-6Al-4V alloy formed at 900°C. Further work has been done to form a superstructure of a design suitable for use in the clinic, but additional work on the fatigue properties of such a component must be conducted to prove its use for patient treatment.

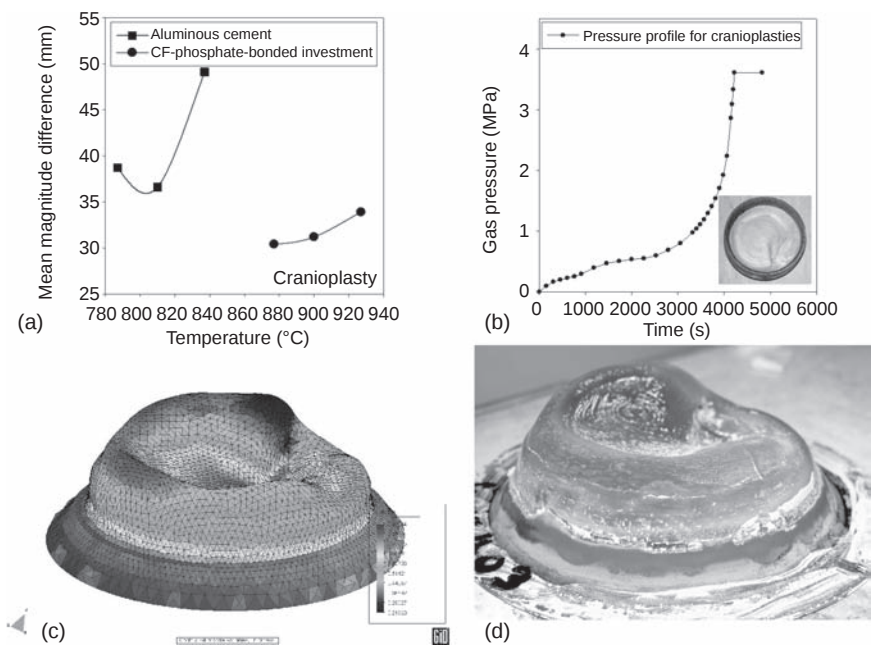
15.6.4 Cranioplasty by superplastic forming

An ABS (Acrylonitrile Butadiene Styrene) master model was built by fused deposition modelling from a modified .stl file captured from CT data as supplied by The Morriston Hospital Swansea. Additional working models (dies) were prepared from this master model using silicone duplicating material and a similar procedure for the implant superstructures. Six dies were prepared for forming at temperatures of 787, 810, 837, 877, 900 and 927°C. SP700 alloy was to be used at the three lower temperatures and Ti-6Al-4V alloy at the three higher temperatures. A Renishaw Cyclone (Renishaw plc, Wotton-under-edge, Gloucestershire) was used to scan the master model and the fit surface of the formed titanium sheet after the cranioplasty had been cut from the formed disc.

The software used to register the scanned surfaces was 3DD Scansurf® (3D Digital Corporation) and Surface Viewer® (Robin Richards, Medical Physics, UCL) was used to output the fit data in the form of histograms such as the one shown in Fig. 15.17a. The magnitude of difference between the formed cranioplasty and the ABS master model as a function of percentage surface considered is shown in Fig. 15.17b. The fit of all the cranioplasties formed at the six different temperatures was excellent by visual inspection and there were no detectable gaps. In order to quantify the misfit it was necessary to use the Renishaw Cyclone™ contacting scanner. Whatever the percentage of the surface of the region of interest chosen to measure fit (Fig. 15.17b), the order of degree of fit of the six cranioplasties onto the master model is the same. The mean magnitude differences are shown in Fig. 15.18a. Figure 15.18a shows that Ti-6Al-4V can be used at a forming temperature within its superplastic range to produce accurately fitting prostheses using a CF phosphate-bonded investment die. The six cranioplasties were formed using the profile in Fig. 15.18b generated using the SuperFlag® program of the University of Wales Swansea (Wood *et al.*, 2001). The similarity between a simulation and a component at the end of a pressure cycle is shown in Fig. 15.18c and d.



15.17 *a* An example of fit data (grey-level scale indicates level if misfit) for one titanium disc formed at 837 °C. *b* Fit of all cranioplasties formed at six different temperatures. AC: aluminous cement; CF: Croform WB investment; PBI: Phosphate bonded investment; DM/D: types of selevest investment.



15.18 *a* Mean magnitude fit of the six cranioplasties to the master model. *b* Pressure profile used for all cranioplasties. *c* Predicted thickness distribution of cranioplasty as output from SuperFlag[®] displayed in GID[™] software package. *d* SPF formed titanium cranioplasty.

15.7 Multiscale simulation of the reactivity and biocompatibility of superplastic titanium alloy prostheses

The motivation for this work was the need to ensure that biocompatibility was not compromised during the manufacture of implantable prostheses by SPF. In the long term, it is envisaged that equations derived from these experimental investigations into the changes in biological response due to specific parameters of the manufacturing process could be incorporated into the existing FE-SPF process simulation software (described in Section 15.3) for the design and manufacture of customised prostheses.

15.7.1 Application to titanium

The goal was to study the interaction between titanium alloy and dental investment ceramic material during the extended high-temperature contact required for SPF, and to gauge the effect of the change in properties and composition on the response of human-derived cells *in vitro*.

The SPF process takes advantage of the properties of certain alloys, notably Ti-6Al-4V, that exhibit large deformation under low applied stress. A process using gas pressure at less than 800psi has been under investigation by the authors for the purpose of forming individually tailored prostheses from Ti-6Al-4V sheet. The die providing the shape is constructed from dental investment ceramic, allowing shapes that fit the patient to be produced using some established dental techniques. The use of argon gas pressure allows the forming of complicated shapes including undercut sections.

Typically, the forming of such shapes takes between 15min and 3h at temperatures ranging from 700 to 950 °C, during which time chemical reactions may occur. Titanium is a highly reactive metal that under normal ambient conditions is protected by a passive oxide film. At high temperatures such as these, the oxide becomes soluble in the metal, and the protection is decreased, so reaction with the substrate is expected to occur.

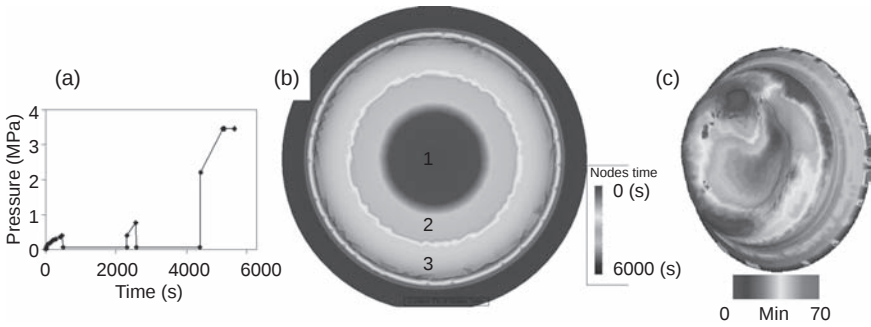
15.7.2 Assessment of surface alteration

A titanium sheet and die geometry was designed to assess the degree of surface alteration of titanium as a function of the time in contact with the ceramic die substrate. Computational simulation was used to predict the contact time at each point and develop a time–pressure profile that would yield the desired contact time profile. To simplify the experiment, a flat substrate was used and only the time–pressure profile was altered to give a pressed titanium sheet with three concentric zones of different contact

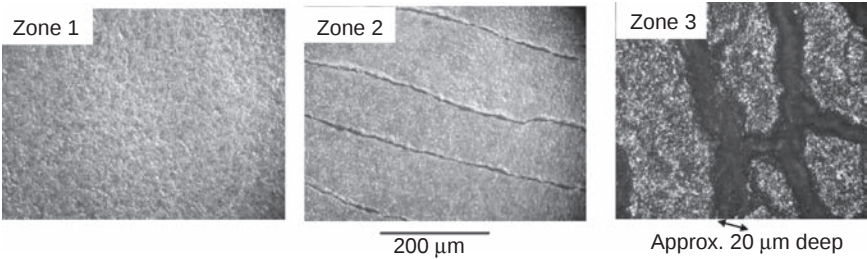
time. The initially flat sheet was formed into a 20mm deep flat-bottomed die, and at three points during forming the pressure was lowered to pause the forming process, as shown in Fig. 15.19a. This resulted in the predicted contact time distribution and sample shape shown in Fig. 15.19b. Similarly, the contact time distribution for an actual cranioplasty prosthesis is predicted in Fig. 15.19c.

The formed sheet was then sectioned into 10mm discs by wire electrostatic discharge machining. Images of the surface of the samples are shown in Fig. 15.20. The dark-field conditions highlight the surface topography.

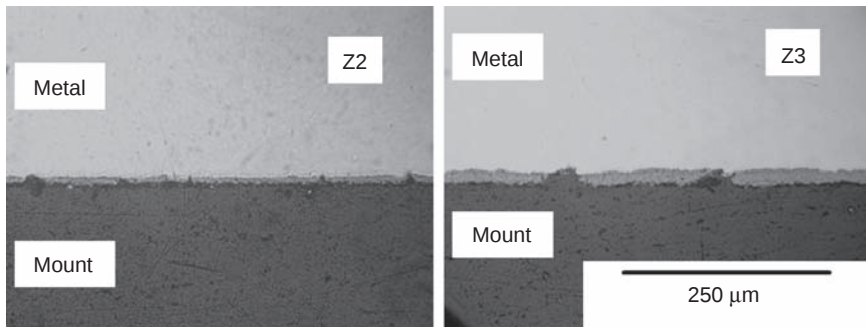
Of particular interest is the observation that the surfaces with less time in contact with the substrate have larger cracks. Metallographic sections reveal a thicker scale layer on the surface in a sample from zone 3 as shown in Fig. 15.21. This led to the conclusion that in this SPF process titanium is protected from contamination when in contact with the substrate. The excess contamination in zone 3 is thought to be due to gases in the forming



15.19 *a* Time–pressure profile and *b* predicted contact times for three-zoned superplastically formed sheet. *c* Contact times during the forming of a cranioplasty implant.



15.20 Dark-field micrographs of the surface of samples from *a* zone 1, *b* zone 2 and *c* zone 3 that were shown in Fig. 15.19b.



15.21 Metallographic cross-sections of the samples from zones 2 (Z2) and 3 (Z3) described in Fig. 15.19b.

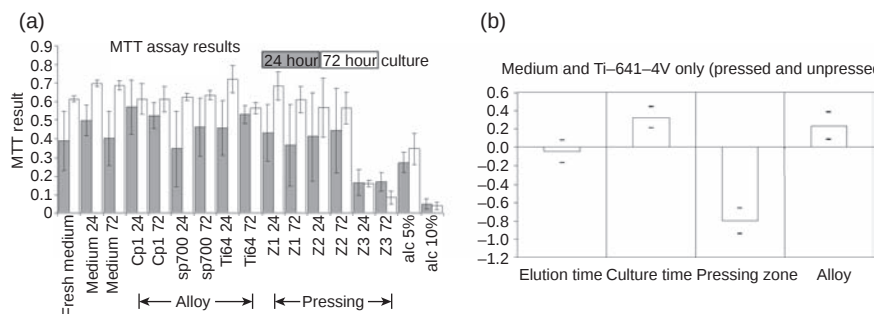
environment, while in zone 1 the contamination from the substrate is significantly less and must occur at lower rates.

15.7.3 Samples for *in vitro* testing

Biocompatibility remains the central theme for biomaterials applications in medicine. A biomaterial is deemed biocompatible if it is free of any severe deleterious effects on the organism and is also biofunctional. Biofunctionality deals with the ability of the biomaterial to perform with an appropriate host response in a specific application.

In order to assess the effect of the contamination, *in vitro* cell culture tests were performed on samples from the pressed sheet. The cytotoxicity of any leachable materials from the samples were tested using the MTT (tetrazolium reduction) assay. This quantifiable test is a measure of metabolic function, and is dependent on the intact activity of the mitochondrial enzyme, succinate dehydrogenase, which is impaired after exposure of cells to toxic surroundings. A human osteosarcoma cell line was used (HOS TE 85 ECACC 87070202) for the indirect cytotoxicity screening. HOS cells were cultured in the presence of eluants from the test materials and exposed to each sample for 24 and 72 h. The results showed that the degree of cytotoxicity decreases with increasing contact time in these samples. Figure 15.22 shows a comparison of these results, and similar results from as-received Ti-6Al-4V similarly sectioned into discs, cell culture medium not exposed to any alloy, and cell culture medium plus 10% ethanol – a known cytotoxin.

It was not expected that oxidised titanium would exhibit cytotoxicity, so it was hypothesised that the deep cracking observed in the outer zone (Figs 15.19 and 15.20) allowed greater contamination from the substrate, even



15.22 Relative cell metabolism assessed with the MTT (tetrazolium reduction) test. *a* Results for several samples including ethanol (alc), fresh cell culture medium and medium agitated for the same time as the elutions, along with unpressed and pressed titanium alloys. Z1, Z2, Z3 refer to the zones described in Fig. 15.19b. *b* Factor effects considering only samples of Ti-6Al-4V alloy and medium alone, illustrating that zone 3 elution (least time pressed against the substrate) has a strong negative effect on the cell metabolism.

though the contact time was less, due to greater adhesion and entrapment of particles of the substrate rather than reaction and diffusion). In order to test this hypothesis, the cytotoxicity of the substrate itself was assessed.

15.7.4 Biocompatibility of the investment material

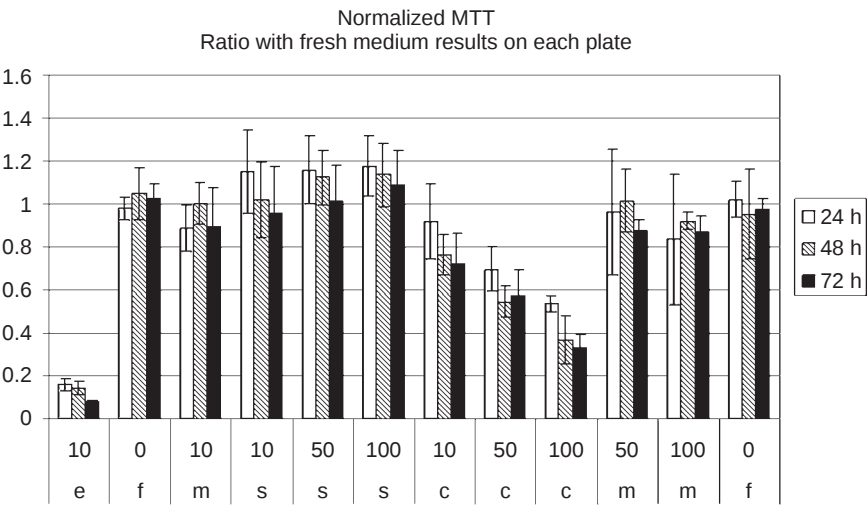
Following SPF pressing, investment material of two types was investigated indirectly for effects on the growth of HOS cells. This was done by testing media agitated with powdered investment material for cytotoxic effects using the MTT test, and directly, by culturing cells on powders placed in the wells of cell culture plates. The latter were assessed using the Alamar Blue (resazurin reduction) test and also by live/dead stain (ethidium bromide/fluorescein diacetate) with fluorescence microscopy. The results shown in Fig. 15.23 seemed to indicate that the leachables from the Croform investment have a consistently negative effect on cell metabolism, increasing with increasing concentration of the elution. However, the Selevest investment did not seem to have the same effect.

15.7.5 Constant-time pressings

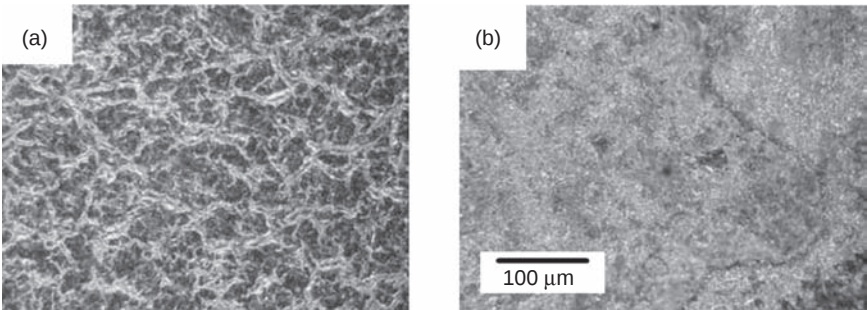
To eliminate the confounding process of the reaction with the surrounding atmosphere, it was decided to use titanium metal pressed with one substrate contact time condition per sheet, by using a pressure profile that formed the Ti-6Al-4V into a 20mm deep, flat-bottomed investment die in approximately 5 min. The pressure was then maintained for a predetermined time

period. Two times were chosen to bracket the range expected for SPF manufacturing of prostheses, namely 20 and 120 min at 900 °C. Subsequently, 10mm discs were cut from these pressed titanium alloy sheets.

Figure 15.24 shows the appearance of the surface of these Ti-6Al-4V samples. Occasional pits were observed on the surface; some investigation into the nature of these pits revealed that they contained some ceramic and



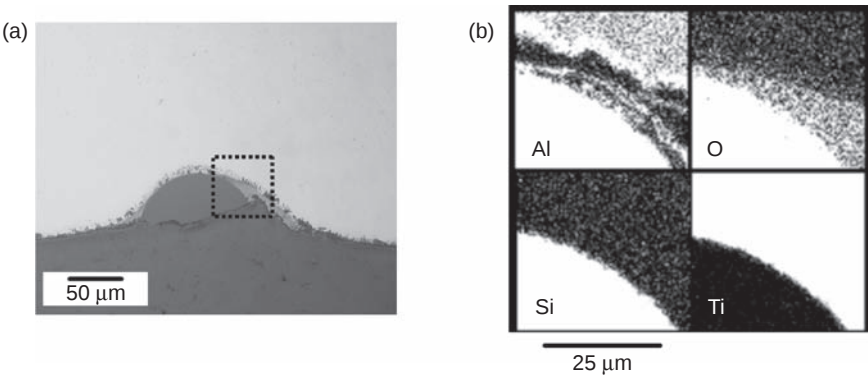
15.23 Relative cell metabolism assessed with the MTT (tetrazolium reduction) test. Letters represent type of material: e, ethanol; f, fresh medium; m, medium agitated for the contact time but without investment; s, Selevest investment; c, Croform investment. The numbers on the horizontal axis represent the amount (in vol.%) of the test substance added to fresh medium before applying to the cell culture. The bars are in the same order as the samples on the plate.



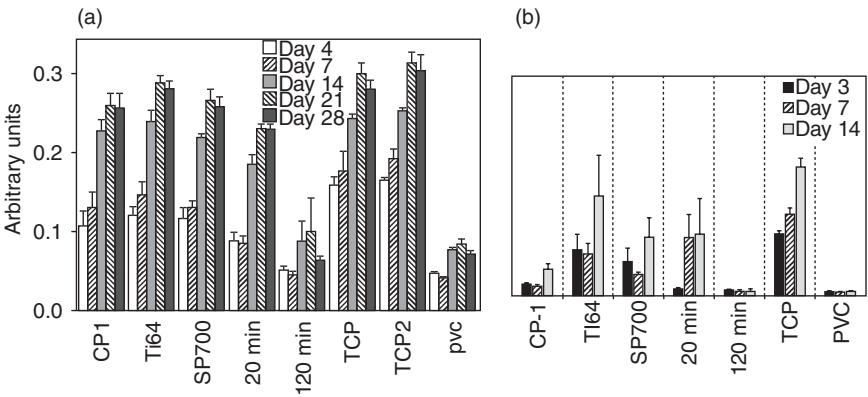
15.24 Surface appearance of Ti-6Al-4V sheet from the a 20 min and b 120 min pressings.

reaction products that contained aluminium and silicon (Fig. 15.25). In this case, the substrate chosen for the experiments was the phosphate-bonded investment (Croform) which does not contain aluminium, suggesting that aluminium from the Ti-6Al-4V alloy has segregated into the reaction products.

The effect of contact between titanium metal and investment on HOB cells *in vitro* is shown in Fig. 15.26. In Fig. 15.26a, the assessment of cell proliferation by the Alamar Blue (resazurin reduction) test showed little difference between unpressed discs of three different titanium alloys: com-



15.25 *a* Cross-section of a sample from the 120 min pressing and *b* EDX elemental map of the (dotted) area. The metal is at the top. Aluminium (Al) and silicon (Si) are present in the reaction zone.



15.26 Assays of the behaviour of cultured cells in contact with the materials. *a* Proliferation assessed by Alamar Blue (resazurin reduction). *b* Expression of alkaline phosphatase in cell lysate assessed by the transformation rate of 4-nitrophenol phosphate to 4-nitrophenol.

mercial purity grade 1 titanium (cp Ti), Ti-6Al-4V, and a modified commercial alloy (SP700) suitable for SPF at lower temperatures than Ti-6Al-4V. The results for Ti-6Al-4V pressed for 20 min are similar with a slight overall reduction in the assay result, which could be due to a smaller number of cells or a reduced rate of proliferation. The results for Ti-6Al-4V pressed for 120 min showed a dramatic decrease in proliferation. In addition, the activity of alkaline phosphatase (ALP), a marker for the differentiation from 'osteoprogenitor' cell phenotype to 'pre-osteoblast' before the formation of mineralizing tissue, was measured. Figure 15.26b shows the activity of the enzyme ALP. It appears that the samples pressed for 20 min reached a peak for ALP expression at day 7, whereas the remaining samples and the control (tissue culture plate without any sample, TCP) exhibited a high peak in activity at day 14. The samples pressed for 120 min were indistinguishable from the known cytotoxin polyvinyl chloride (PVC) samples. Both sets of results indicate that the presence of reaction products on the surface has a cytotoxic effect but also has a stimulatory effect on cell differentiation.

15.7.6 Research impact and benefit of superplastic titanium prostheses

The greatest research impact of this work is that we have come to understand that while investment materials were formerly expected to have a detrimental effect on the surface characteristics of SPF titanium, we now consider them to be actually beneficial in two main respects. The first is that the investment materials tested have a role in protecting the surface from contamination with air during SPF forming, in that they prevent cracking of the surface. The second effect concerns the biocompatibility and the enhanced response of human osteoblast cells as indicated by the alkaline phosphatase assay of SPF titanium that had been in contact with investment material for 20 min. The obvious benefit to society is that SPF is a good process for forming complex and customisable implant shapes, even on relatively low-cost investment materials, but it has also been shown that patients requiring implants could benefit from the surface modification that takes place at the same time. Ultimately, we intend to exploit additional titanium surface-die interactions to modify surfaces for enhanced hard and soft tissue coverage following implantation.

15.8 Future trends

In this chapter, we have explored the use of SPF for medical and dental prostheses. In a world where customisation is becoming increasingly important, the demand for implants that are more customised is seen to be

beneficial to the performance and longevity. SPF could become a niche manufacturing tool for certain types of customised prostheses especially since the combined advantages of low forming pressures, low-cost tooling, high dimensional accuracy and appropriate surface modification could make the process comparatively cost effective. An important aspect of the application of SPF to the medical and dental sectors is the development of sophisticated modelling tools based on finite element and geometrical simulation. The combined package is a powerful tool that will enable manufacturers to deliver customised components in a predictable manner. Further developments are expected in this field, including die shape optimisation based on the geometry of the required prosthesis and the use of laser-based heating sources to complete most stages in the superplastic hot forming operation, including further surface modification where needed (<http://www.listechnology.com>).

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Dental investment materials for casting metals and alloys

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16.1 Introduction

2007 marked the centenary of dental casting by the lost wax process for tooth restoration. In 1907, Dr William Henry Taggart, a Chicago dentist presented his research to the New York Odontological Society (Taggart, 1907). Production of a wax pattern, investing, burn-out and centrifugal casting were described. Today's practice can be traced to that publication. Unfortunately for Taggart, less than 15 years later, a paper revealing prior discovery was found in the dental library at the University of Iowa. Dr B. J. Philbrook, a Denison dentist, had reported gold casting for dental restoration to the Iowa State Dental Society at Des Moines (Philbrook, 1897). Although Taggart's technique was more complete, patents were revoked. Nevertheless, Taggart's achievement deserves recognition for establishing dental casting as we know it.

Through the twentieth century, the technique was refined, initially to obtain accurate and detailed dental gold castings, then to repeat this success for higher fusing cobalt- and nickel-based alloys. Requirements for the investment material are established, agreed and listed in any dental student textbook. Investment materials developed in the first half of the twentieth century meet these requirements in general, to give clinically acceptable dental castings. A substantial volume of research was published in this period. More recently, the attention of researchers has concentrated on other materials (such as an amalgam replacement). Patient demand has driven the commercial imperative and academics have been attracted to these other materials to enjoy a higher research profile. Wrongly, many assume that dental casting investment materials have reached a level of development that makes them completely fit for purpose and that the technology is stable. This is not the case. Casting titanium and the requirement for increased precision have given new challenges. In recent years, unresolved issues on silica-based phosphate-bonded casting investment material and solving the problem of casting titanium have dominated publications and are the main focus of this chapter.

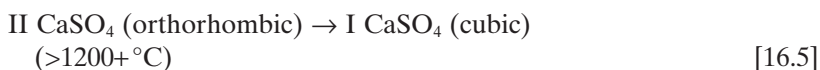
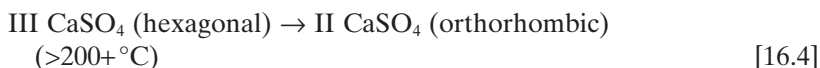
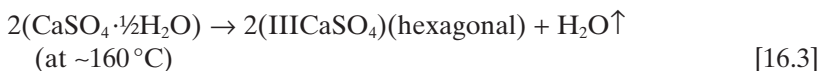
16.2 Chemistry and structure of binders in established silica-based dental casting investment materials

16.2.1 Gypsum-bonded material

The chemistry of this material was investigated several decades ago. It sets by crystallisation:



When heated, evaporation of the excess water required for mixing takes place between 60 and 100 °C, followed by the loss of water of crystallisation. With further heating, the structure of the anhydrite changes from hexagonal to orthorhombic.



Higher setting and thermal expansions are recorded when stone replaces plaster. Stone produces a workable mix at a lower water–powder ratio, hence a denser set structure. Although the mould is heated in air, a localised wet environment is created in the initial stage of burn-out, more so if the mould still contains a significant part of the excess water required for effective mixing. A dense set structure and wet environment favours the formation of stone when the mould is heated (equation [16.2]). After the remaining water of crystallisation has been lost, the transformation of the anhydrite from III CaSO₄ to II CaSO₄ takes place more rapidly and at a lower temperature when stone has formed during heating (of the mould). The matrix contracts less as a result of the denser structure and rapid transformation (Mori *et al.*, 2003).

Empiric development led to small additions of boric acid and sodium chloride to reduce shrinkage resulting from the loss of water of crystallisation during heating. In the localised wet environment in the first stage of dehydration (equation [16.2]), the presence of sodium chloride favours the formation of stone. This accelerates the transformation of the anhydrite

from III CaSO_4 to II CaSO_4 (equation [16.4]), which is completed 200 °C lower than normal. The denser structure resulting from stone formation and rapid transformation lead to less contraction in the matrix during heating. Unfortunately, most of the gain appears transient. Sintering decreases the difference between modified and unmodified materials. The action of boric acid is different. Upon heating, it decomposes to B_2O_3 which inhibits evaporation of the last water of crystallisation to prevent the prompt initiation of the III CaSO_4 to II CaSO_4 transition and suppress densification of the porous structure (Mori, 1986).

As an additive, boron has other uses. The cast surface on some precious alloys is discoloured. Although the reaction product, CuO , can be removed by pickling, preventing its formation would be preferable. An addition of a powdered reactive element, such as boron, to the investment powder can achieve this. It would be misleading to suggest this is totally effective since black CuO is replaced by the less conspicuous red Cu_2O . At the level required to be effective, 0.2%, all properties with the exception of strength are unaffected. Strength is increased, attributed to B_2O_3 acting as a sintering agent. While higher strength is a bonus, it may not be significant (Kakuta *et al.*, 2003; Nakai *et al.*, 2003; Meng *et al.*, 2004a).

An addition of up to 1% fine polytetrafluoroethylene (PTFE) particles will prevent the undesirable loss of fine investment particles during production of the investment (Horiuchi *et al.*, 1996). On burn-out, PTFE decomposes to form HF as an intermediate compound which reacts immediately with the calcium sulphate.



The calcium fluoride is believed to coat the anhydrite to produce a more refractory matrix, thereby eliminating gas evolution from anhydrite decomposition at the surface in contact with the molten alloy. Less than 1% PTFE is sufficient to overcome the manufacturing problem but insufficient to confer improved mould surface properties. If a low addition of PTFE is selected, substituting 2–40% of the silica with a more stable oxide, nitride or carbide restores the surface improvement.

16.2.2 Phosphate-bonded material

Set investment

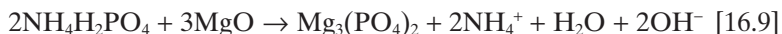
All commercial dental products utilise the reaction of a blend of $\text{NH}_4\text{H}_2\text{PO}_4$ and MgO powders mixed with water. Allan and Asgar (1966) positively

identified struvite (crystalline $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) in the set investment and proposed a simple reaction to account for its formation.



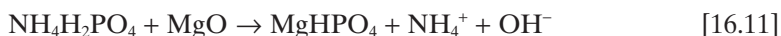
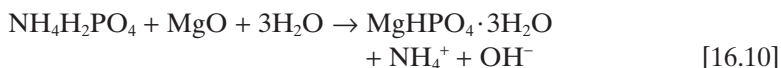
Nieman and Sarma (1980) confirmed its presence and provided a mechanism for its formation. The acid phosphate dissolves rapidly and saturates the solution, thereby lowering the pH which leads to dissociation of the magnesia. As a consequence of that dissociation the pH rises and colloidal struvite particles form to produce setting by gel formation. More recently, Soudee and Pera (2000) have proposed an alternative mechanism in which nucleation of struvite takes place on the surface of the magnesia particles (not in the body of the liquid), and grows outward using hydrated magnesium ions from solution. When the magnesia surface is fully covered with a monolayer of hydrated magnesium ions $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, magnesium ions can no longer be released, a point that corresponds with setting. This model allows acid phosphate, magnesia and struvite to co-exist in the set material and provides an explanation for Allan and Asgar's (1966) comment that co-existence is possible since some of the magnesia is non-reactive.

In addition to recording the presence of struvite, ^{31}P solid-state Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectroscopy has revealed the existence of amorphous $\text{Mg}_3(\text{PO}_4)_2$ (Scrimgeour *et al.*, 2007a, 2007b). A lack of crystallinity does not prevent positive identification of a structure by solid-state MAS-NMR spectroscopy, as it does when using x-ray spectroscopy.



The existence of a fine amorphous $\text{Mg}_3(\text{PO}_4)_2$ structure and the absence of $\text{Mg}_3(\text{PO}_4)_2$ peaks in x-ray powder diffraction spectra are consistent with the proposition that a gel forms first during setting. Across a product range, amorphous $\text{Mg}_3(\text{PO}_4)_2$ and struvite are present in variable amounts and either can dominate. Since a manufacturer is able to formulate an effective dental casting investment product with considerable freedom, it is not surprising that this freedom is reflected in a variation in the relative amounts of each phase.

The exotherm from the main setting reaction produces a temperature rise which is dependent upon product formulation and affected by differences in mould volume, mixing equipment and ambient conditions. It appears that a different rise can lead to conditions that are favourable to the formation of other phases. In some products, amorphous MgHPO_4 and newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) have been detected by ^{31}P solid-state MAS-NMR spectroscopy.



Since solid-state MAS-NMR spectroscopy gives information on structure at an interatomic level, a microstructure with distinct and homogeneous volumes cannot be assumed when two or more structures are recorded. Crystalline newberyite had not been reported previously. As it is present in a minor amount, it might not have registered above the ragged saw-tooth background in the multi-peaked x-ray diffraction spectrum. However, it is known to be the binding compound formed when an alternative to $\text{NH}_4\text{H}_2\text{PO}_4$ is used in dental casting investment (Takashiba *et al.*, 2002) and exists in related civil engineering cements (Sugama and Kukacka, 1983).

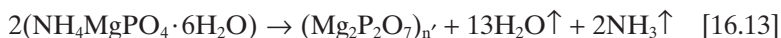
In theory, it is possible to employ acid phosphate compounds other than $\text{NH}_4\text{H}_2\text{PO}_4$ as a reactant in dental phosphate-bonded investments. Health and safety concerns about the release of hot ammonia gas during burn-out has prompted research on an ammonium-free replacement (Zhang *et al.*, 2001; Takashiba *et al.*, 2002). Therefore, $\text{Mg}(\text{H}_2\text{PO}_4)_2$, preferably pre-dissolved in water, produces an investment with potential. Newberyite forms as a binding matrix. A setting expansion of 2% is available, but over-reliance upon setting expansion is questionable since it is associated with anisotropic expansion.



The mould surface that sets in contact with silicone duplicating material can have a salt-like crust of crystalline alkali metal phosphates which adversely affects the accuracy and detail of the cast. Its formation can be prevented by the presence of an organic acid such as citric acid in the investment powder. However, the organic acid has an adverse effect on other properties and a zeolite is a more suitable alternative (Schwabe *et al.*, 1996).

Burnt-out material

In general, the results of x-ray powder diffraction spectroscopy and differential thermal analysis have been interpreted to identify structures and temperatures at which they exist. With the progressive loss of water of crystallisation and ammonia, an amorphous ionic glass, $(\text{MgP}_2\text{O}_7)_n'$ forms. Its existence was hypothesised from the x-ray powder diffraction spectra obtained at temperatures either side of the range within which the glass occurs (Nieman and Sarma, 1980). This range varies from study to study, but there is general agreement on 300–620 °C (Nieman and Sarma, 1980; Higuchi *et al.*, 1982a, 1982b).



As the temperature increases further, this ionomeric structure is replaced by crystalline magnesium pyrophosphate.



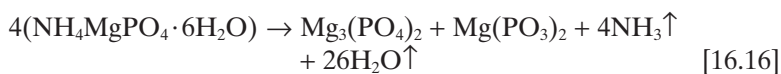
At higher temperatures, excess magnesia reacts with the magnesium pyrophosphate to produce crystalline magnesium orthophosphate, farringtonite and a two-phase pyrophosphate/orthophosphate structure.



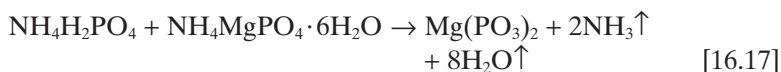
The temperature at which this commences is also inconsistent between studies: above 600 °C (Higuchi *et al.*, 1982b), 750 °C (Nieman and Sarma, 1980) or 1300 °C (Higuchi *et al.*, 1982a).

Although crystalline magnesium metaphosphate can be formed by heating a mixture of unreacted MgO and $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ powders (Higuchi *et al.*, 1982b), x-ray powder diffraction spectral lines have not been seen when set dental phosphate investment material is burnt-out (Allan and Asgar, 1966; Nieman and Sarma, 1980; Higuchi *et al.*, 1982a; Wakasa and Yamaki, 1992). However, metaphosphate peaks are present in ^{31}P solid-state MAS-NMR spectra (Scrimgeour *et al.*, 2007a). If the structure is glassy, x-ray powder diffraction and MAS-NMR spectra are consistent.

Thermal decomposition of struvite can produce a mixture of meta- and ortho-phosphates. A two-compound structure has been found in some burnt-out investment products by applying ^{31}P solid-state MAS-NMR (Scrimgeour *et al.*, 2007a).



Magnesium metaphosphate can be formed also by P_2O_5 (released by the thermal decomposition of any ammonium dihydrogen phosphate that remains after setting) reacting with struvite or the minor constituent newberyite in the set investment. The net effect being:



Metaphosphates are characterised by a PO_4^{3-} tetrahedron sharing two oxygen atoms with adjacent tetrahedra (Wells, 1962), which leads to a variety of ring and linear structures.

A lower burn-out temperature appears to favour the formation of magnesium metaphosphate together with minor quantities of farringtonite (Scrimgeour *et al.*, 2007a). The appearance of crystalline farringtonite at the expense of some of the amorphous orthophosphate is the result of devitrification. Both ^{31}P solid-state MAS-NMR and x-ray powder diffraction spectroscopy agree that at high burn-out temperatures pyrophosphate and orthophosphate are present (Nieman and Sarma, 1980; Higuchi *et al.*, 1982a, 1982b; Scrimgeour *et al.*, 2007a). Magnesium pyrophosphate could reform at the expense of both magnesium metaphosphate and magnesium orthophosphate through a simple reaction:



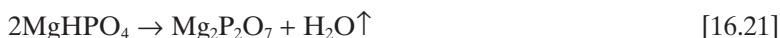
Once the metaphosphate has been consumed, orthophosphate will be formed by the reaction of the magnesium pyrophosphate with magnesia (equation [16.15]). At the limit to which the material is usually heated (1000–1300 °C), magnesium pyrophosphate may remain in the structure (Higuchi *et al.*, 1982a; Scrimgeour *et al.*, 2007a) or may be replaced totally with magnesium orthophosphate (Nieman and Sarma, 1980; Higuchi *et al.*, 1982b).

Product-specific amounts of sodium, calcium and zinc are present. These elements are not normally associated with textbook setting reactions and may result from different levels of impurity in the source for magnesia or undisclosed additives. In many products, calcia is present in a significant amount (3–30%), seemingly as an additive and not an impurity. Calcia might produce improvements in the performance of refractory or binder. There are several possibilities, but in the absence of definitive evidence speculation is not advisable. Compounds, formed by additives or impurities during the later stages of burn-out, that soften or melt at lower temperatures than the phosphate or silica could be the cause of greater plasticity during casting (Luk and Darvell, 1997a). The benefit of up to 5% boron nitride to prevent reaction between the investment and nickel alloys has been demonstrated. Cast surfaces were smoother, brighter cast and did not adhere to the mould (Wakasa and Yamaki, 1991).

Decomposition of ammonium-free investment is similar to that of conventional commercial products (Zhang *et al.*, 2001; Takashiba *et al.*, 2002). Heating leads to the loss of water of crystallisation and a contraction above 160 °C. Naturally, ammonia is not released.



Further contraction is attributed to the formation of pyrophosphate.



Integrity of the mould is a concern when there are large volume changes over narrow temperature ranges. In this case, it may not be an issue since significant strength (~ 15 MPa) is retained after burn-out. The net thermal expansion at the 900°C burn-out temperature is low, just 0.2%. Ultimately, casting accuracy is the proof of concept, which is still due.

16.3 New investment materials – responding to the challenge of casting titanium

16.3.1 The problem of casting titanium for dental use and strategies to resolve this

Casting titanium for dental applications has acted as a major spur to investment development. Titanium presents two major problems; a high melting point (1670°C) and high reactivity. The unsuitability of silica-based phosphate-bonded moulds has been illustrated by Takahashi *et al.* (1990) and by Yan and Takahashi (2006). To reduce the degree of surface reaction, but retain some thermal expansion, the mould is cooled before casting. Even at a reduced temperature an unwanted hardened surface layer extends to a depth of about $200\mu\text{m}$ on the casting. In theory, an increase in setting expansion could compensate for the reduction in thermal expansion. In reality, this is a high-risk strategy and the development of a new investment is a more promising solution than pursuit of alternatives to the expansion lost by casting into cool moulds.

In more conservative products, an alumina/magnesia base is adopted and the phosphate binder retained. Other products employ entirely new chemistries for both binder and refractory. There is no consensus on which chemistry will become dominant. Even if a particular chemistry produces an acceptable investment material, it could become redundant through market preference for another. Table 16.1 lists casting investment products that have been recommended for titanium casting. This list is not intended to be all-inclusive. Its purpose is to illustrate recent diversity.

There is an alternative and apparently simple solution. Place a thin layer of material more stable than titania on the internal surface of the mould. The wax pattern is coated with the compound then invested in conventional silica-based phosphate-bonded investment. Thus, existing alloy shrinkage compensation remains available. However, care must be exercised if silica sol is used in the investment mix. It can penetrate the thin and porous inert barrier.

A number of oxides have been investigated, either to replace silica in the investment or to form the protective barrier. Table 16.2 lists their stability, according to the Gibbs free energy of formation (ΔG_{oxide}), calculated at the most relevant temperature, the melting point of titanium. The feasibility

Table 16.1 Dental casting investment materials recommended for titanium casting

Product name	Manufacturer	Base	Binder
Biotan Vest MG	Schutz-Dental Group, Rosbach, Germany	SiO ₂ , MgO	Phosphate
T-invest CB	GC Corp., Tokyo, Japan	SiO ₂ , Al ₂ O ₃	Phosphate
CD titan	Shofu Inc., Kyoto, Japan	Al ₂ O ₃ , ZrO ₂	Phosphate
Titanium Vest EX	Ohara Co., Osaka, Japan	Al ₂ O ₃ , ZrO ₂	Phosphate
Tancovest	Bego, Bremen, Germany	SiO ₂ , MgO, Al ₂ O ₃	Phosphate
Titanium Vest	Ohara Co., Osaka, Japan	SiO ₂ , MgO, Al ₂ O ₃	Phosphate
Rematitan Plus	Dentaurum, Ispringen, Germany	SiO ₂ , MgO, Al ₂ O ₃	Phosphate
T-invest C&B	GC Corp., Tokyo, Japan	SiO ₂ , Al ₂ O ₃	Phosphate
Titavest MZ	J Morita Mfg Corp., Osaka, Japan	MgO, Al ₂ O ₃ , MgAl ₂ O ₄	Phosphate
Selevest D	Selec Co., Osaka, Japan	MgO	Aluminous cement
Selevest CB	Selec Co., Osaka, Japan	MgO	Aluminous cement (with Zr)
Titavest CB	J Morita Mfg Corp., Osaka, Japan	MgO, Al ₂ O ₃ , ZrO ₂	Spinel
Titavest ME	J Morita Mfg Corp., Osaka, Japan	MgO, Al ₂ O ₃	Spinel
Biotan Vest C&B	Schutz-Dental Group, Rosbach, Germany	MgO, Al ₂ O ₃	Spinel (with Li(OH) ₂ solution)
Biotan Titan	Schutz-Dental Group, Rosbach, Germany	MgO, Al ₂ O ₃	Spinel (with magnesium acetate/alcohol solution)

for the reduction of the oxide in contact with molten titanium can be determined from these data.



If reduction is possible, the free energy for the reaction [16.24] will be negative. Only silica is susceptible to breakdown (see Table 16.2).

Table 16.2 Thermodynamic properties of oxides used in dental casting investment materials and mould surface coatings. Values of ΔG are calculated from data given by Kubaschewski and Evans (1965). $\Delta G_{\text{feasibility}} = \Delta G_{\text{titania}} - 2/y$. ΔG_{oxide} for an oxide with the formula M_xO_y (see equation [16.24]). Reduction of the oxide titanium is feasible when this has a negative value.

Oxide	Gibbs Free Energy of formation at 1943 K ΔG_{oxide} (kJ mol ⁻¹)	Feasibility for reduction by titanium at 1943 K $\Delta G_{\text{feasibility}}$ (kJ mol ⁻¹)	Melting point (K)	Melting point of titanium + melting point of the oxide
CaO	-557	+269	2973	0.69
MgO	-569	+293	2943	0.68
SiO ₂	-790	-55	1986	0.97
TiO ₂	-845	0	2193	0.91
ZrO ₂	-987	+142	2973	0.65
Al ₂ O ₃	-1573	+611	2303	0.87
Y ₂ O ₃	-1742	+949	2683	0.72
MgAl ₂ O ₄	-2187	+497	2408	0.82

Thermodynamic data are obtained using pure and stoichiometric compounds. With comparatively impure commercial compounds used in investments, it is possible to get a trace reaction.

A third proposal is to accept an inadequate expansion of a casting investment material provided it is consistent and predictable. Full compensation for metal contraction could be created during production of the wax pattern. Dental computer aided design/computer aided manufacturing (CAD/CAM) allows oversize wax patterns to be cut with great precision. This would allow the chemistry of the investment to be optimised for low reactivity (Zhang *et al.*, 2006).

16.3.2 Surface reaction on dentally cast titanium

Whichever refractory base and binder are employed, a hardened surface layer appears to exist. A general structure can be described. Up to four zones form the hardened surface layer – reaction zone, α -case zone, inhomogeneous zone and acicular needle-shaped α -grains in prior β -grain boundaries (Luo *et al.*, 2002; Meng *et al.*, 2004b; Atwood *et al.*, 2005). A normal cast structure lies below this hardened layer. There are product-specific differences that can be understood by reference to this general model and composition of the investment material.

Consider the casting of titanium into a silica-based phosphate-bonded mould. All four zones are present and the hardened surface extends to its greatest depth compared with that produced by any other investment. Pure titanium solidifies at 1670°C as β -titanium and transforms to α -titanium at 882°C. Reaction with the mould alters solidification, transformation and microstructure, to a depth at which contaminants from the investment can diffuse. The temperature of titanium entering the mould will be about 1750°C, to ensure the mould is filled before solidification commences. When the molten titanium comes into contact with the investment, a friable titania scale a few micrometres thick will form (Wang *et al.*, 1998). This reaction zone is removed during the normal deinvesting and sand-blasting procedures. Reduction of the investment leads to solution of the constituent elements (oxygen, silicon, phosphorus, magnesium), to become contaminants in the surface metal after solidification. Oxygen, interstitial and the predominant contaminant, stabilises α -titanium (in which it is soluble up to 32%) to the extent that α -titanium can form directly from the liquid as an α -case up to 25 μm thick. Silicon, a substitutional element (relatively insoluble in α -titanium), segregates to liquid between growing α -titanium dendrites, thereby creating a second zone. Detailed analysis of this inhomogeneous zone reveals the presence of three phases – α -titanium, β -titanium and Ti_3Si (Papadopoulos *et al.*, 1999). Since silicon is more soluble in, and stabilises β -titanium, the presence of β -titanium is not surprising. This zone in which silicon is non-uniformly distributed is present to a depth of 50 μm (Atwood *et al.*, 2005). Being interstitial, oxygen can diffuse to a greater depth. Beyond the limit to which silicon can diffuse acicular α -titanium grains exist within prior β -grain boundaries, indicating solidification as β which transforms to α on cooling. The presence of oxygen is presumed to favour acicular grains since a normal equiaxed cast structure is found below them, at depths beyond the diffusion limit. Hardening is attributed to the presence of the dissolved oxygen to a depth of 200 μm (Papadopoulos *et al.*, 1999; Luo *et al.*, 2002; Meng *et al.*, 2004b; Atwood *et al.*, 2005).

At the other extreme, when an yttria coating is present on the internal surface of a mould made with low-reactivity investment, only the acicular grains exist to any notable extent and the hardened layer is at a minimum thickness.

Hardening at the surface of dentally cast titanium is the sum of two effects. Firstly, contamination, primarily by oxygen from reaction with the investment, and secondly, an altered cast microstructure at the surface. Realisation that the extent of the hardened layer depends on normal reaction kinetics led to casting into moulds held at 300°C or lower. Rapid cooling of the metal reduces the opportunity for reaction. This adaptation in the dental casting process is now established. The temperature of the mould is just one factor. A larger casting volume results in slower cooling,

which allows greater diffusion of elements and in turn increases the thickness of the hardened layer. Even with a low mould temperature the hardened layer might be 75 μm on a thin section but double that on a thicker section. The layer might change in thickness, but its structure is maintained. The volume of the casting, contamination by the investment and the temperature of the poured alloy, affect the microstructure, particularly the size of the acicular grains (Oda *et al.*, 1996; Meng *et al.*, 2004b; Atwood *et al.*, 2005).

16.4 Surface coating the internal surface of the mould

Stable oxides such as alumina, zirconia or yttria can be applied as a powder to the surface of the wax pattern to create a low-reactivity barrier separating the mould from the molten metal. Either conventional or new investment can be used. Complete protection is claimed when zirconia slurry is used (Wang *et al.*, 1998; Papadopoulos *et al.*, 1999). This may be optimistic since other evidence suggests coatings reduce but do not eliminate the reaction (Oda *et al.*, 1996; Luo *et al.*, 2002; Koike *et al.*, 2003; Atwood *et al.*, 2005). Solution of the elements from the coating and investment still occurs though their concentration in the surface is more limited (Oda *et al.*, 1996; Koike *et al.*, 2003). A zirconia surface coating applied as slurry halves the surface layer thickness (Koike *et al.*, 2003); yttria is more effective. The method of application affects performance; dry spraying the pattern with yttria powder is not as effective as slurry application (Wang *et al.*, 1998).

A zirconite ($\text{SiO}_2 \cdot \text{ZrO}_2$) coating is effective (Luo *et al.*, 2002), limiting the hardened layer to 75 μm . Oxygen remains the predominant contaminant in an α -case. Silicon (from the coating and investment) is retained in the liquid when the α -titanium nucleates and grows. In time, other structures form below the α -case to accommodate a higher silicon content (β -titanium and Ti_3Si). Zirconium, the other substitutional contaminating element, simply decreases progressively with depth since its solubility limit in α -titanium exceeds the concentration present.

16.5 The chemistry of new investment materials

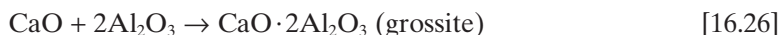
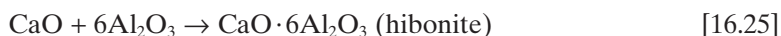
16.5.1 Magnesia- and alumina-based phosphate-bonded investment materials

In general, the chemistry of the binder is the same as that for silica-based investment. At least four refractory oxides have been used to replace some or all of the silica. The reaction with a magnesia-/alumina-/silica-based investment (Rematitin Plus[®]) releases aluminium into the molten titanium. An α -case forms to a depth of $\sim 20 \mu\text{m}$, confining the aluminium

(an α -stabiliser). Silicon segregates ahead of this, concentrating in a zone extending to 70 μm . The hardened layer is limited to the depth to which oxygen can penetrate. A third zone of oxygen-containing acicular α -titanium grains takes the hardened layer to a total of 200 μm (Atwood *et al.*, 2005). The microstructure produced by silica-/alumina-based investment (T-invest CB[®]) is similar. Silicon, aluminium, phosphorus and oxygen are found in the first 50 μm with acicular grains extending to a depth of 150 μm (Oda *et al.*, 1996; Watanabe *et al.*, 1997; Meng *et al.*, 2004b). The same microstructure results when CD-titan[®] is used. However, silicon is not a contaminant since this is an alumina-/zirconia-based product (Oda *et al.*, 1996).

16.5.2 Alumina-based gypsum-bonded investment materials

Ultimately, silica-based gypsum-bonded investment is limited by the reaction between anhydrite and silica. The temperature for this breakdown is usually taken to be around 1250 °C. If alumina replaces silica the resulting investment material has a low, but usable set strength and the same setting expansion (−0.5%) as that of silica-based material. When this experimental investment is heated to a conventional burn-out temperature, contraction from decomposition of the gypsum exceeds thermal expansion to give a net contraction. Fortunately, if heating is continued to 1200 °C, the anhydrite decomposes and the calcia that is created reacts with alumina to form two crystalline mixed oxides:



These reactions produce an expansion of 3%, which can be adjusted by altering the alumina–gypsum ratio; 4:1 appears to be the optimum. Most of this reaction expansion is retained when the mould is cooled. However, the strength of the cooled burnt-out material is very low (Yan and Takahashi, 1998). A blend of magnesia and alumina powders (1:6) as the refractory phase, with 2% solution of K_2SO_4 in place of water, refines the chemistry. The setting expansion becomes very low (0.03%) which is seen as a positive feature since the overall expansion is less anisotropic. The reaction temperature increases to 1400 °C and the reaction leads to 2.4% expansion. Titanium can be cast to an acceptable accuracy with the mould at room temperature, answering the question as to whether its strength is sufficient. Reaction between the mould and hot metal is reduced, though not eliminated. Such improvement is expected, given the presence of highly stable Al_2O_3 , CaO and MgO (Yan *et al.*, 2004). Sulphur dioxide will be released when the alumina-based investment is heated (as it is from overheated

silica-based investment). No information is available on whether it is a problem.

16.5.3 Magnesia-based silica-bonded investment materials

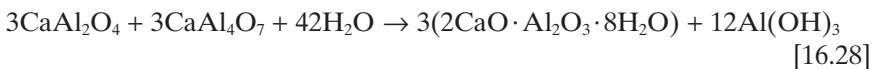
Magnesia- (Wakasa and Yamaki, 1995) and magnesia–alumina–zirconia- (1:1:trace) (Wakasa and Yamaki, 1994) based experimental investments have been developed to cast titanium. It is surprising that silica was chosen as a binder considering that oxides more stable than silica replaced it as the refractory phase. Setting is accompanied by contraction. A low thermal expansion would be anticipated since neither magnesia nor alumina possess the inversion expansions of silica. Nevertheless, the investment expands up to 1% at the burn-out temperature of 900°C. To minimise surface reaction the mould is cooled to 70°C and cast at that temperature. At first, it is difficult to reconcile an acceptable fit for a titanium crown casting with an expectation of no setting and trivial thermal expansion. Though speculative, a reaction seems the obvious cause of expansion. At 830°C, there is a strongly exothermic reaction between these oxides, which results in the formation of orthorhombic enstatite.



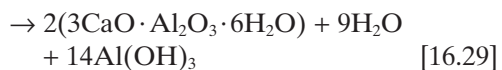
Thus, reactivity of the investment could be reduced and if enstatite formation is accompanied by expansion, this will be retained on cooling with the potential for accurate castings.

16.5.4 Magnesia-based aluminous cement-bonded investment materials

An investment with this chemistry is available commercially, Selevest D®. Since the investment contains about one-third aluminous cement binder, negligible change on setting should be anticipated. Aluminous cement was developed through the twentieth century for civil engineering, in which application near-zero dimensional change on setting is a prerequisite. Aluminous cement contains equal quantities of two components, calcium aluminate and calcium dialuminate. Mixed with water, they dissolve to release Ca^{2+} , $\text{Al}(\text{OH})_4^-$ and OH^- ions. Hydrates precipitate almost immediately to produce setting:



Over time, this octahydrate converts to a hexahydrate:



The time between setting and burn-out is unlikely to be sufficient for this conversion. Selevest D[®] contracts during setting. When heated, the cement dehydrates which offsets thermal expansion and, at the 900 °C burn-out temperature, the result is a small net expansion. If the mould is cooled to room temperature for cold casting, changes in the binder during the burn-out leave a net contraction, 0.32% (Kitahara *et al.*, 2004). Others have confirmed a seemingly inadequate expansion for Selevest D[®], contracting 0.07% on setting and expanding to a net 0.13% on heating to burn-out at 700 °C (Soo *et al.*, 2001). A binary experimental investment (85 MgO:15 aluminous cement) has a net 0% change at burn-out (700 °C) then contracts 0.9% on cooling to room temperature (for casting) (Zhang *et al.*, 2006). Contraction is inherent to the system.

To overcome this deficiency, 2.7% zirconium powder has been added. (Product names Selevest DM[®] and Selevest CB[®] appear in the literature. The difference, if any, is not given.) The setting contraction remains unchanged, 0.04% (Soo *et al.*, 2001). However, between 550 and 700 °C, the investment expands rapidly, to 1.1% for Selevest CB[®] (Hung *et al.*, 2004) and to 1.4% for Selevest DM[®] (Soo *et al.*, 2001) due to oxidation. Nearly all of this expansion is retained when the mould is cooled to room temperature for casting. Mixing appropriate proportions of zirconium-free and zirconium-containing variants has been proposed to adjust the expansion (Soo *et al.*, 2001).

Other reactive additives could be used to the same effect. Experimental zirconium carbide or nitride additions to Selevest D[®] produce expansion though oxidation (Kitahara *et al.*, 2004). For casting titanium, the optimum addition is 3.3% ZrC or 4.9% ZrN. Although the rapid expansion during reaction reduces strength (presumably by microcrack formation), the strength appears to be adequate. Surprisingly, a non-reactive addition can expand the aluminous cement binder when heated. Adding 5% zirconia to the zirconium-containing product Selevest CB[®] increases the thermal expansion by 0.5% (a 45% improvement) by a mechanism that has yet to be determined (Hung *et al.*, 2004).

α -Stabilisers, aluminium and oxygen, are to be found in a thin α -case on titanium cast in a Selevest CB[®] mould. As expected, fine acicular grains extend hardening to a depth of 100 μ m. Raising the mould temperature from 100 to 200 °C coarsens acicular grains significantly, but does not alter the hardness profile which suggests that the presence of this structure and not its refinement is the key factor (Meng *et al.*, 2004b). As might be expected, a further increase in mould temperature increases the depth to which aluminium can diffuse, thickening the α -case (to 30 μ m) although the total surface-hardened-layer thickness remains unchanged (Koike *et al.*, 2003).

16.5.5 Alumina–magnesia-based spinel-bonded investment materials

Titavest CB[®], intended for casting titanium, is a blend of 70% MgO, 25% Al₂O₃ and 5% ZrO₂ which is mixed with a 30% magnesium acetate solution containing 5% ethanol. An undisclosed but small addition of ZrN is present to aid thermal expansion. (It is a flexible chemistry. Other formulations are available for refractory model production: Titavest ME[®], 80% MgO, 20% Al₂O₃; Titavest MZ[®], 50% MgO, 25% Al₂O₃ and 25% MgAl₂O₄.) The mould expands 1.2% as it sets. Upon heating, decomposition of the binding compound causes a contraction until the spinel (MgAl₂O₄) forms at 880°C whereupon the investment expands rapidly to 1.3%. Cooling to the 600°C casting temperature reduces the expansion to 1.0%.

Commonly, spinels are produced by co-precipitation using mixed acetates (or nitrates) followed by calcination. A patent, assigned to K. K. Morita of Kyoto, for a spinel-binder dental casting investment discloses a chemistry (Ogino and Nishimura, 1990). At least 10% of the particles in a mixture of magnesia and alumina powders are less than 100µm in size. These ‘fine’ particles give a reactive powder, which dissolves when mixed with water leading to the formation of hydroxides. The process is enhanced if magnesium acetate solution is used in place of water. As the mix ‘hardens’ it expands. Heating to 600°C leads to formation of the spinel. The mould can be cooled to 150°C for casting. Striking similarities point to the use of such a chemistry in the commercial product (Titavest), although this is not proof that it has been used.

After burning out, a Titavest MZ[®] mould contains magnesia and spinel but not alumina (Oda *et al.*, 1996). Oxygen is reported as the only contaminant in an α-case that has a significant thickness, 50µm (Meng *et al.*, 2004b). Formation of spinel during burn-out to make the investment less reactive is a feasible explanation for the absence of dissolved metals. This contrasts with the discovery of Oda *et al.* (1996), who found aluminium, magnesium and silicon as well as oxygen contamination to a depth of 30µm in titanium cast into a hot (700°C) mould. It suggests that spinel can be reduced by molten titanium even though the thermodynamic prediction is stability (Table 16.2). Lowering the mould temperature reduces contamination although aluminium can still diffuse to a depth of 5µm when a Titavest CB[®] mould is at room temperature (Syverud *et al.*, 1995). There is agreement that acicular α-titanium grains are formed below the α-case to complete the hardened layer. If the mould is cold they extend to a depth of between 80µm (Syverud *et al.*, 1995) and 125µm (Meng *et al.*, 2004b). If hot they extend further, to 200µm (Meng *et al.*, 2004b).

16.5.6 Calcia-based lost resin-bonded investment materials

Dispersing the refractory powder in a monomer to produce an investment that sets by polymerisation is a radically different approach. Organic binder and wax pattern burn off together, after which sintering provides cohesion. This pre-existing technology (for the production of crucibles) has been adapted to give a calcia-based experimental investment containing 78% CaO, 2% CaF₂ and 20% methylmethacrylate monomer. The autopolymerised acrylic binder gives a composite with adequate set compressive strength (~22 MPa) and burns off completely by 400 °C. Unfortunately, polymerisation produces a setting shrinkage which sintering worsens. Calcium fluoride is required as a sintering agent. If absent, the strength after burn-out is inadequate. Closure of pores by sintering increases strength at the expense of greater shrinkage; a compromise is necessary. Sintering at 900 °C avoids excessive contraction and produces low but acceptable strength. To create the expansion required for an accurate casting, titanium powder is present in the investment. There is an expansion when it oxidises at 700–900 °C. A 6% inclusion leads to an expansion of 1.7%, which is retained on cooling to room temperature to allow casting into a cold mould. Absorbed oxygen creates a hardened surface layer, an α -case, overlying acicular grains. The effect (if any) that the fluoride has on the cast titanium has yet to be determined (Nakai, 2000, 2002; Meng *et al.*, 2004b).

16.6 Effect of the hardened surface layer upon the properties of a titanium dental casting

A hardened surface layer is considered undesirable with the potential to affect key properties. At the time when casting titanium for dental uses was first considered, the investment materials available were not fit for the purpose. New investments have improved matters. The effect on properties should be reviewed to consider whether the residual layer still presents a problem.

The chemical composition of the layer is a factor in corrosion resistance. Its composition changes with the investment used, by virtue of elements picked up from the mould. Better corrosion resistance results from casting into a magnesia-based mould than one that is silica based (Cai *et al.*, 1999). Casting into a mould that has a high-stability oxide (zirconia or yttria) coating on the mould walls does not result in better corrosion resistance than is obtained by casting directly into a mould with a stable oxide base (Watanabe *et al.*, 2004). Whereas the presence of a hardened surface layer produced by casting into magnesia-based investment might by its chemistry make no difference to corrosion resistance, the greater surface roughness

accompanying its formation gives lower corrosion resistance (Koike *et al.*, 2003). A finishing procedure that smoothes the surface gives a significantly better corrosion resistance even without the total removal of the hardened (contaminated) surface layer. It follows that corrosion behaviour can be influenced as much by the finishing process as by the presence and composition of the surface layer (Cai *et al.*, 1999).

The hardened layer has no effect on machinability (Ohkubo *et al.*, 2006) and does not alter cytotoxicity to any significant extent (Watanabe *et al.*, 2004). However, it is more brittle and may contain cracks (Meng *et al.*, 2004b). Subsurface porosity can form when some investments are used (Wang *et al.*, 1998; Meng *et al.*, 2004b). There may be a higher risk of fracture and less corrosion resistance compared with titanium that has not been cast, but the relatively low level of the difference makes the cast material clinically acceptable.

16.7 Issues concerning silica-based phosphate-bonded investment

16.7.1 The continuing problem of setting expansion

For some silica-based phosphate-bonded products, the setting expansion is particularly sensitive to the mixing method (Taira *et al.*, 2000). Change in the growth and morphology of the struvite crystals formed during setting is an obvious explanation. The cause is multi-factorial with mixing ratio, temperature, mixing time, mixing speed and air pressure influencing the result. While it is possible to specify the temperature and mixing ratio, the other factors are characteristics of the mixing equipment, which makes it difficult to reproduce the setting expansion (between laboratories) with any degree of certainty. Placing mixers in an order according to the expansions produced in the setting investment is inconsistent from product to product (Lloyd *et al.*, 2004). Taira *et al.* (2000) state,

It seems important to set specific mixing conditions including the P/L ratio and mixing time for a combination of each investment and each mixing machine. The mixing condition which is recommended by the manufacturer is not always applicable and best suited to every dental mixing machine. When changing the mixing machine it seems necessary to calibrate the mixing condition for each investment used.

This is an important observation. It implies that the manufacturer should not give a numerical value for setting expansion and puts the onus upon the technician to adjust his/her casting procedure if he/she elects to buy a new product, using trial and error castings until a satisfactory result is achieved. This may well reflect existing practice in dental laboratories,

but it is far from a satisfactory position. Given the number of mixer models on the market, it would be an excessive burden to expect the manufacturer of an investment product to produce a comprehensive list of settings. Two practical alternatives exist. First, the manufacturer could specify settings for selected mixers and the corresponding expansions. There is a precedent for this; the instructions for use that accompany amalgam products give trituration times for a limited number of amalgamators. The second alternative is to remove the problem by developing binders with near-zero setting expansion and rely upon thermal expansion alone.

The absence of constraint at the end of the mould leads to a vertical expansion that is similar to free expansion (Earnshaw *et al.*, 1997; Takahashi *et al.*, 1999). Horizontal expansion is constrained, thus less. In all cases, the effective expansion has to be considered in both horizontal and vertical directions. They may differ significantly. Compressibility of the lining and absence of constraint at mould end surfaces assist expansion while the wax pattern and casting ring constrain expansion. Inhomogeneous expansion is expected, but becomes a major concern only when the setting expansion is large.

Internal constraint arises from the rigidity of the pattern material when the pattern surrounds part of the investment, as in the core of the mould for a crown. Since a wax pattern constrains only part of the mould (i.e. material that is surrounded by the pattern), the question of inhomogeneous expansion arises. As much as 80% of setting expansion will be lost in an investment core that is surrounded by a wax pattern (Earnshaw and Morey, 1992a, 1992b). Investment in the core of a crown patterned in soft inlay wax expands in a ratio of 5:3 (vertical:horizontal). This ratio changes to 15:1 when more rigid acrylic pattern resin is used (Takahashi *et al.*, 1999). Consequently, there could be negligible setting expansion over much of the fitting surface of an acrylic pattern. This calls into question the reliance on setting expansion when a rigid pattern material is used. There is a further complication. Beyond the gingival line, there is no pattern to constrain the expansion and expansion in the region of the gingival line increases to match that of the main body of investment, creating 'flaring' on the casting.

16.7.2 The measurement of strength

Convenience and pre-existing testing practice for silica-based gypsum-bonded products led to the adoption of room temperature compression testing for determining the strength of silica-based phosphate-bonded material. Invariably, the strength of set material is quoted. With some justification, this can be described as inadequate. The material is brittle

and susceptible to tensile failure. Room temperature is not the temperature at which in-service failure takes place and the composition of the binder changes during burn-out. Knowledge of the strength before burn-out has a value, but this is limited to events experienced by the mould at that stage alone. There is a belief that room temperature strength can be used as a guide to high temperature strength. As for any belief, evidence – no matter how slim – is cited to justify this. The simple truth is that room temperature compressive strength is not a reliable guide to fracture strength at burn-out temperature. The rank order of products is not the same at each temperature (Luk and Darvell, 1991). This underlines the inappropriateness of room temperature measurements (Earnshaw *et al.*, 1997; Chew *et al.*, 1999).

Is the strength of this investment more than sufficient or, in some cases, too great? Significant underestimates for strength (by using low-temperature values) have led to a suggestion that it is unnecessary to take this into account since lower strength gypsum-bonded moulds have sufficient strength for casting and it follows that such a strength should be sufficient for phosphate-bonded moulds, as well (Chew *et al.*, 1999). A combination of high strength and a non-linear shrinkage coefficient will restrict shrinkage of the metal at higher temperatures, thereby creating a potential distorting mechanism. This has led to a call for the introduction of products with lower hot strength (Earnshaw *et al.*, 1997). Reformulation to the advantage of other properties could be considered even if the consequence is a fall in strength.

Deficiencies inherent in conventional strength testing are removed by adopting the disc rupture test introduced by Luk and Darvell (1991). The disc-shaped specimen is set horizontally in a dental casting mould. Cylindrical cavities either side of the disc do not extend to the circumference of the disc. The upper cavity is sprued. After the mould is heated and burnt-out, the alloy is melted and cast into the mould using a centrifugal casting machine. Molten metal enters the mould on one side of the disc and applies a force according to the mass selected. If the force is sufficient, the disc ruptures by tensile loading. This test has one limitation. It is unsuitable for temperatures less than 400 °C since wax must be burnt-out completely. This limitation is acceptable since 400 °C is below temperatures relevant to failure in-service. Although production of each specimen for this disc rupture test is more time consuming and the number of specimens is greater, the test is conducted under conditions that simulate the service state precisely (temperature, specimen size, loading rate, stress state). Technical correctness that gives rise to a valid result must outweigh questionable simplification for the sake of easy testing. The utility of the disc rupture test has been confirmed by independent evaluation (Juszczyk *et al.*, 2002).

In general, as the burn-out temperature increases (above the 400°C lower limit for the test), the tensile (disc rupture) strength falls due to progressive decomposition of the binder and the quartz $\alpha \rightarrow \beta$ transformation. A minimum strength is reached, beyond which strength may increase significantly. This rise is attributed to magnesium orthophosphate formation. Beyond 900°C densification by sintering increases the strength. Although a degree of commonality exists between products, variation of strength with temperature is product-specific resulting from differences in formulation, sourcing of constituents, additives and impurities (Luk and Darvell, 1997a, 1997b). The relative strength of products differs at the burn-out temperature compared with that at room temperature (Juszczak *et al.*, 2002).

It is important to distinguish between the temperature to which the mould is heated (burn-out or casting temperature) and the actual temperature experienced by the investment. The molten alloy might be 100°C higher than the investment. Consequently, the inflowing liquid will raise the temperature significantly. The part of the mould in contact with the metal is at an elevated temperature for a time sufficient to allow the investment to deform plastically before solidification (Luk and Darvell, 1997a). Such deformation also occurs in silica-based gypsum-bonded moulds (Luk and Darvell, 2003). Melting of the investment in contact with the molten alloy has been seen (Juszczak *et al.*, 2002). This begs the question: is there inherent inaccuracy in all castings from such deformation when a silica-based investment mould is used to cast a high melting point alloy? Fortunately, although the answer is yes, in most cases the magnitude of the deformation is within the casting tolerance for removable metal-frame prostheses (Juszczak *et al.*, 2007). However, despite this positive outcome, there is still cause for concern when the required accuracy is greater than that which is acceptable for a partial denture.

Handling technique has a marked effect on strength (Juszczak *et al.*, 2000). Mixing protocols and procedures before setting that minimise porosity produce a set investment that has greater and more reliable strength. Large pores initiate fracture. Eliminate these and fracture must be initiated by other structural features that have the ability to act as stress concentrators, features such as large refractory particles. It follows that combining an investment with a finer particle size and a technique that eliminates porosity should lead to greater strength. As with setting expansion, strength is dependent upon structure and affected by the same mixing variables. Surprisingly, there is no correlation between compressive strength and setting expansion (Taira *et al.*, 2000)!

The fracture toughness (K_{IC}) of silica-based phosphate-bonded products has been calculated assuming crack initiation at the largest visible pore (size = a) and applying the relationship with stress (σ_F) derived from linear elastic fracture mechanics, $\sigma_F = K_{IC} (\pi a)^{-0.5}$. In their set state, three products have

values 3.0, 3.2 and 5.3 MPa m^{0.5} (Juszczyk *et al.*, 2000). Compared with dental porcelain ($K_{IC} = 1.2\text{--}2.0\text{ MPa m}^{0.5}$) or fully sintered alumina ($K_{IC} = 4\text{--}6\text{ MPa m}^{0.5}$) these values might overstate the fracture toughness of the investment. The methodology can be criticised, but these are the only published values for dental casting investment materials and stand until contradicted.

There is a strong case for adopting changes universally. Strength should be measured at both room temperature and at the burn-out temperature. The heating produced by the molten alloy should be added to the burn-out temperature. The investment is a brittle material and a form of tensile loading is required to replace the compression test. Ideally, the fracture toughness (K_{IC}) should be measured directly.

16.8 Rapid casting

Until relatively recently, most (perhaps all) technicians believed that slow or incremental mould heating is necessary to avoid cracking. Products that withstand rapid heating are available today, to be used in a rapid (also known as an accelerated) casting technique. Typically, a silica-based gypsum-bonded mould can be placed directly in a burn-out oven set at 750 °C 30 min from the start of mixing, held there for a further 30 min and then cast. The cycle is reduced from 6 h to 1 h, an obvious attraction. Rapid heating without fracture is made possible by the presence of both cristobalite and quartz in the investment. This combination reduces the rapid inversion expansions that must be accommodated at each temperature (Murakama *et al.*, 1994). The control of setting expansion has to be a concern. At 30 min, the investment is still expanding at a significant rate. Obviously, the oven insertion time has to be defined with some precision for each product, and adhered to. For silica-based gypsum-bonded products intended for rapid casting, it seems advisable to have a low setting expansion to minimise the effect of variability.

In common with gypsum-bonded products, rapid casting has been applied to silica-based phosphate-bonded products. Since phosphate-bonded investment sets rapidly, it is possible to reduce the bench holding time to 15 min, by which time the peak in the setting exotherm has passed. Crowns produced this way have an acceptable fit (Konstantoulakis *et al.*, 1998; Schilling *et al.*, 1999; Yan and Takahashi, 2006). There appears to be no difference in the fit of castings made by the conventional and rapid casting techniques. The choice of product has a greater effect than the technique employed (Yan and Takahashi, 2006). Products have been formulated specifically for rapid casting. In addition to increasing the quartz:cristobalite ratio, metal powder has been included by one manufac-

turer with the intention of reducing the temperature gradient in the mould. Although there are tailored products, it may be possible to use conventional products. If this is attempted, expect to modify elements of the procedure; for example, explosive cracking can occur at the end of the mould, but effective countermeasures are available (Konstantoulakis *et al.*, 1998; Schilling *et al.*, 1999).

16.9 Conclusions

Far from being a stable technology, dental casting investment material is still undergoing a sea change in formulation. The casting of metallic restorations and implant components in substantial numbers continue to make this material a key element in dental technology. CAD/CAM offers an alternative method for fabrication, but does not have the flexibility with cost effectiveness of lost wax casting. The requirements set many years ago hold true to this day. While the two types most widely used today (silica-based gypsum-bonded and silica-based phosphate-bonded) perform well, it is clear that improvements are still possible. For example, the setting expansion of phosphate-bonded material is very sensitive to restraining force, technical manipulation and environment – to the extent that the International Organization for Standardization (ISO) technical committee for dentistry has not set a requirement in the standard since the interlaboratory variability was unacceptable. The development of products that do not rely upon this expansion would be desirable. However, in the hands of competent operators who use consistent techniques, both types perform more than adequately, given the low level of complaint. Perhaps, the greatest and most recognised issue with users is deterioration of powder left exposed to the environment for some time. Arguably, this problem is user created and user solvable. Once a package is opened it must be resealed and the seal must be moisture-proof. The manufacturer's packaging is required (by the ISO standard) to prevent the entry of moisture into resealed packages. Packages suitable for a single mould should be used if deterioration is an issue in the laboratory. Casting titanium presented a significant challenge which appears to have been met by new chemistries. Minimal surface reaction has been achieved with expansion by reaction adding to that of setting (if it is available).

ISO publishes standards for dental products that are adopted as national standards in many countries; notable among these are nations in the European Union. In 1999, alarmed at the ever increasing number of standards across all areas, the European Committee for Standardization (CEN) requested all of its technical committees to examine the standards in their respective areas with a view to combining existing standards. Dentistry had three standards for casting investment materials (for gypsum-,

phosphate- and ethyl silicate-bonded products), each dating from the product type entering general use. Once feasibility was shown, detailed work on combining these (together with standards for the closely related refractory die materials) was undertaken within the ISO technical committee for dentistry (ISO TC106). A new standard – ISO15912. 2007; *Dentistry – casting investments and refractory die materials* – was published in 2007, to replace five existing ISO standards. Compared with the obsolete standards, it contains changes to harmonise text and procedures as well as revisions to reflect current knowledge and understanding. This development has a consequence that was peripheral to the original remit, but clearly has considerable importance. All products, without regard to chemistry, are now within the scope of an ISO standard for casting investment material. There is no bar to products with new chemistries seeking to comply with the ISO standard, to give the consumer an assurance that the product is fit for purpose. Thus, the centenary of Taggart's publication has been marked by a very significant development.

16.10 Acknowledgement

This contribution is dedicated to Professor Dick Earnshaw who passed away in 2006. This recognises his great achievements in the field and his legacy in Australian and ISO standards for dental casting investment and refractory die materials.

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